ENHANCING LIGHT-ENDS RECOVERY THROUGH JOINT ATMOSPHERIC DISTILLATION OF HEAVY CRUDE AND USED ENGINE OIL

BY

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Declaration

I, Momoh Omuya Raheem, declare that the work in the dissertation entitled **'**Enhancing Light-Ends Recovery through Joint Atmospheric Distillation of Heavy Crude and Used Engine Oil' has been performed by me in the Department of Chemical Engineering, under the supervision of Professor A.S. Ahmed, Dr. I.A. Mohammed-Dabo and Dr. C.S. Ajinomoh.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at any other university.

Momoh Omuya Raheem		
.....	.....	.....
Name of Student	Signature	Date

Certification

This dissertation entitled **"**ENHANCING LIGHT-ENDS RECOVERY THROUGH JOINT ATMOSPHERIC DISTILLATION OF HEAVY CRUDE AND USED ENGINE OIL" by Momoh, Omuya Raheem meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello, University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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Dedication

I dedicate this work to my late aunt, Mrs Maryamoh Lawal. Mama, it's since 1985 that you left this world to a greater beyond, but the big legacy you left behind through the support of your late husband (Mallam Lawal Aroke) is the love that you extended to all the people that have had contact with you and especially to your younger brother (my father, late Mallam Momoh Ajagu Animoku Avajara) and indeed, my late mum, Mrs. Aminetu Momoh. Many if not all the people you left behind can attest to this fact. Mama, I wouldn't say that without you, I wouldn't have been lettered, because of destiny from Almighty God. However, I can reasonably convince others that God has used you as the pillar to that effect and on this account alone, I shall remain grateful to God that I came across somebody like you in my life. Your memory will linger in my heart till I return to meet you in the eternal kingdom of God. May your soul rest in perfect peace. Amen

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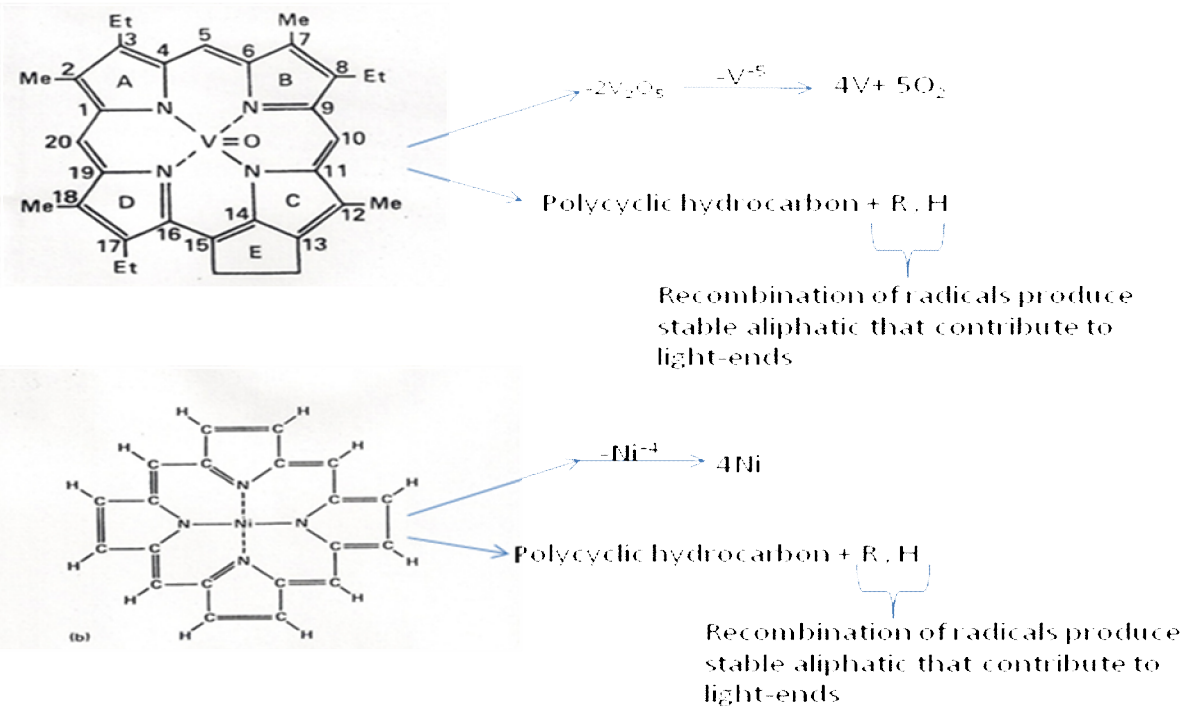
Last but not the least, I wish to appreciate the understanding and support that my beloved darling wife, Mrs. Vivian Nana Hawawu Onyianame Momoh and my children have shown while I am not at home trying to bring this work to its conclusive end. May love, peace and harmony continue to wax stronger in our life.

Abstract

Heavy crude oils are known to contain significant amount of high molecular-weight substances such as asphalthenes and resins hence, when refined, produce low amount of light-ends (gasoline, kerosene and diesel fractions). Compared with light crude oils, as a refinery feed stock this singular reason coupled with difficulty of processing has made heavy crude oil business unattractive at local and global levels. In this work, enhancement of light-ends recovery by joint atmospheric distillation of Venezuela, Mixed (50% Venezuela and 50% Antan wt./wt.) and Antan heavy crude oils blended with used engine oil (UEO) was investigated. This was carried out by subjecting these blends to spectrophotometric analysis for optimal feed choice and subsequently acted as basis for true boiling point (TBP) distillation process. The results show that blended Venezuela heavy crude with 1% UEO which corresponded to maximum particle size of blend and 12% UEO corresponding to minimum particle size of the blend enhanced the recovery of light-ends by extra 1.8% and 0.74% respectively. Similarly, blended Mixed heavy crude with 16% UEO (max. particle size of blend) and 4% UEO (min. particle size of blend) enhanced the recovery of the light-ends by 2.32% and 2.25% respectively. Finally, blended Antan heavy crude with 19% UEO (max. particle size of blend) and 7% UEO (max. particle size of blend) enhanced the recovery of the light-ends by 7.42% and 1.76% respectively. All these confirm that on the average, the larger the particle size of the blend the higher the chance of enhancement of the recovery of the light-ends.

However, the undefined pattern (i.e. positive and negative enhancements) of the product slates of the fractional cuts prompted the need for further AAS analyses to check for the presence of freed 3d-metals (V, Ni, Co, Fe.) from their complexes in the residues of the blends. This was to confirm whether the enhancement was partially as a result of light cracking of the

resin/asphalthenes (preferably porphyrins and porphins) and other organometallic compounds that could have been originally present in the crude. The sequence of probable mechanism of the light cracking is presented thus:



Since this type of cracking is of uncontrollable mechanism it underscored the reason why the pattern of the distribution of the products was difficult to establish. While the free radicals formed may recombine to yield gaseous product (methane, ethane, etc.) or light distillate like naphtha/ kerosene fraction, it may as well yield heavier fractional cuts like vacuum distillate.

Used engine oil must have only provided enabling environment for these transformations to take place because it must have reduced the energy of the bonding of crude oil micelle, hence enhanced the recovery of the light-ends.

Key Words: **Heavy Crude Oil** **Used Engine Oil** **Light-ends** **Enhancement** **Blends** **Asphalthene** **3d-metal Complex** **Porphyrin**

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LIST OF SYMBOLS AND ABBREVIATIONS

a(N) - first correction function of the zero base-lines of EPR spectra

B- total flow rate of bottoms, kgmol/h

b(N) - second correction function of the zero base-lines of EPR spectra

B_0 - the electron's magnetic moment, T

c(N) - third correction function of the zero base-lines of EPR spectra

Cr - the amplitude of a EPR spectrum

D - total flow rate of the distillate, kgmol/h

D_1 and D_2 - absorbance index

D - average particle diameter of crude oil, m

g - average degree of association of the individual molecules that constitute a system

g_e - electron's so-called g-factor

h - Planck's constant, Js

H_{ji} - enthalpy of each pure component *i* in the vapor stream leaving plate *j*, kJ/kg

h_{ji} - enthalpy of each pure component *i* in the liquid stream leaving plate *j*, kJ/kg

L_o- reflux, kgmol/h

L_0/D=reflux ratio

M_{as}- molecular mass of the associate

N_A-Avogadro number, mol^{-1}

P- Total pressure of the system, kPa

P_i - the vapor pressure of pure component *i* at the temperature *T* of the system, kPa

P^L - total pressure throughout the liquid phase, kPa

P^v - total pressure throughout the vapor phase is equal to the, kPa

q- heat required to vaporize one mole of feed divided by the latent heat of vaporization of the feed, kJ

Q_c,- net amount of heat removed per unit time by the condenser, kJ

Q_R - the net amount of heat introduced to the reboiler per unit time, kJ/h

R - gas constant, $JK^{-1}mol^{-1}$

S - the specific surface area, m^2/g

X- concentration of the spins in the EPR sample

V_1 - overhead vapor, kgmol/h

$x_{i,}$ - the mole fractions of component i in the liquid phases

y_i,- the mole fractions of component i in the vapor phases

Greek Letters

γ - surface tension, mNm^{-1}

δ_2 - solubility parameter, g/ml

ΔE_η - energy of activation of kinematic viscosity, Joules

ΔH^v - heat of vaporization, kJ

η - dynamic viscosity, cP

λ – wavelength, nm

μ_B - Bohr magneton, JT^{-1}

ρ - density of particles in dispersed phase (g/m^3)

Abbreviations

AAS- Atomic absorption spectrometer

API- American Petroleum Institute

ASTM- American Society for Testing and Materials

CDS- Colloido- dispersion system of crude oil

EFV- Equilibrium flash vaporistion

EGS- Enhance Geothermal System

EPR - Electron Paramagnetic Resonance

ESR - Electron Spin Resonance

(5-95) Gap, Separation criteria for adjacent products cuts in a column

IBP - Initial boiling point

PW- Petawatts (10^{15}Watts)

RAC - Resin-asphalthenic compounds

SAE- Society of Automotive Engineers

SI - second integral of the EPR spectrum

TBP - True boiling point

UEO - Used engine oil

CHAPTER ONE

1.0 INTRODUCTION

The world proven reserve of crude oils is about 1.243 trillion barrels, and at daily rate of consumption (http://en.wikipedia.org/wiki/oil_reserves, 2009) of 2.6%, it is believed to be able to last mankind for the next 54 years. Nigeria is joint contributor to this reserve as it ranks 6th among the Organisation of Petroleum Exporting Countries (OPEC) and 10th in the world. Her reserve is put at about 36 billion barrels (OPEC DATA, 2008).

At global level crude oil business is mostly centered on conventional or light crudes, such as Bonny lights, Escravos lights, Arabian lights, Venezuela lights etc. On the contrary, very little attention is paid to heavy crudes (see Figure 2.3) because of the perception that their light distillate content (gasoline, kerosene and diesel fractions) is very low and apart from that they are relatively difficult to process. Unfortunately, light crude oil reserve is fast depleting (Swain, 1997).

The declining reserves of light crude oils have resulted in an increasing need to develop options to upgrade the known heavy crude oil reserves in order to obtain more light ends from them (Speight, 1999). Many researchers believe that this can be achieved through many external influences, such as thermolysis, photolysis (Ajinomoh, 2005), acoustic sound on the crude or its blending with hydrocarbon additives before distillation (Petrakov, 2000; Mohammed, 2001).

In this research work, the last option is considered by investigating the use of used engine oil (UEO) for upgrading some heavy crude oils. The role of used engine oil in this work is fundamentally based on the theory that it can partially reduce the bonding energy of the crude oil micelle thereby availing its components (especially porphyrins and other organometallic compounds in the core region) to 'effective' distillation process (Saidakhmedov *et al*, 1986).

1.1 RESEARCH PROBLEMS

Most of the world's current source of crude oil supply is conventional crudes (mostly light crudes). It is so because compared with the heavy crudes, light crudes are relatively easier to process, thus justifying a high return on investment from them.

Unfortunately, the reserve of light crude oils has been reported to be in the decline since the last two decades and apart from this their price is relatively high and usually very unstable for any reasonable economic planning and projection at national as well as at global level. As reported by Khan and Partmore (1997) this has prompted the need to technically develop the available heavy crude oils for refining schemes.

In this work used engine oil which is usually considered as waste and agent of environmental pollution has been chosen to be a useful material for blending with heavy crudes in order to enhance the recovery of light-ends (gasoline, kerosene and diesel) in them. In this way the issue of sustainable development and economic value of heavy crudes and used engine oil would be feasible.

1.2 AIMS AND OBJECTIVES

This project is aimed at enhancing light distillates recovery in atmospheric distillation of crude oil. The specific objectives are:

1. To investigate the use of used engine oil as blending additive in enhancing light ends in the distillation of heavy crude as feed stock.
2. To study the role of particle size (micelle) of the crude or its blend in the prediction of product slates.

3. To investigate the role of porphyrins (d-metals complex) in the long residue, in order to establish their level of contribution to this enhancement.

1.3 JUSTIFICATIONS

This work is very significant and relevant to some of the stake holders (producer, marketers, equipment designers and distillation unit operators) in oil business at local and global levels. In this context, marketers will take the advantage of low price (http://www.businessweek.com, 2008) and abundant reserve of heavy crude (OPEC DATA, 2008) for a fairly good return on investment as presently obtained in light crudes counterpart. Except introduction of blending equipment in the atmospheric distillation unit there will be no reason for any major unit operation equipment reconfiguration. The used engine oil which will be employed to carry out the enhancement of the recovery of the light ends is 'waste' and abundant (Momoh *et al*, 2005).

Similarly, the negative impact of used engine oil on the environment and human health would be curtailed.

1.4 SCOPE

The work involved materials collection like the sourcing of desalted and dewatered Venezuela and Antan heavy crude oils from Kaduna Refining and Petrochemical Co. Ltd and the Department respectively. The specific gravity of the two samples and the mixture were generated for their suitability for the research work. The next step was the procurement of used engine oil from mechanic workshops and filling stations for characterization (Momoh *et al*, 2005) purpose. This was followed by data generation from particle size measurements of the blends and

fractional cuts after the pure crudes and selected blends have been subjected to true boiling point (TBP) distillation exercise. The final action was the data analysis of the residues in order to check the role of decomposed porphyrin (d-metal complexes) in the enhancement of the light ends in the distillation process.

1.5 LIMITATION

The role of porphyrin in this work would have been clearer established through the use of analytical equipment like electron paramagnetic resonance (EPR) or electro spin resonance (ESR) machine, but due to unavailability, atomic absorption spectrum (AAS) machine was used as a replacement.

CHAPTER TWO

2.0 LITERATURE REVIEW

Though energy may be hard to define precisely, but it is very familiar to all of us. Most of the energy we need to live and work with is supplied to us through the food we eat. We need other fuels too: wood, natural gas, oils, gasoline, etc., for cooking, warming our homes, or moving our vehicles. For thousands of years, man used the energy released by burning fuels for such purposes as keeping warm and, on a small scale, as an aid to his arts and crafts. Until only recently all heavy works were done by muscles, either human or animal. Since the Industrial Revolution, however, man has been using more and more energy from other sources to replace muscular effort. Burning fuels now supply most of the energy needed to operate our farm machinery, run our factories, drive our trains, automobiles, ships, and our planes, etc. The energy taken from fuels is an absolute necessity to our present technical society. In fact one very good measure of technological progress and material wellbeing of a country is the average amount of energy taken from fuel for each season during the year (Anonymous, 1965). In essence, the energy consumption of a nation is very big factor in measuring the gross domestic product (GDP) of the citizens.

Current global and local energy profiles and prospects would be discussed in due course, but, however the major challenge mankind is facing is the issue of sustainable development of his resources as heavily campaigned in the 1992 Kyoto Protocol of United Nations Organisation (UNO).

Therefore, this research work is focused on a sustainable method of processing and managing some heavy crude oils and used engine oil respectively. Hitherto, while the former used to be considered as not too valuable materials in energy businesses, the latter was always considered as ‘waste’.

2.1 GLOBAL ENERGY PROFILES

Contrary to the belief of some, the world is not running out of energy, nor is it rapidly running out of crude oil. The problem is of different dimension: it is to find and gain access to new reserves of energy before existing sources decline too far. Within the context of this work the author wishes to situate heavy crude oil and used engine oil in the global energy profiles viz-a-viz its resources, production and consumption with special emphasis on how they can be sustainably used in order to complement the existing energy resources.

2.1.1 World Energy Resources

Most of the world's energy resources are from the sun's rays hitting the earth (http://en.wikipedia.org/wiki/File:Breakdown_of_the_incoming_solar_energy.svg,2008, 2010). Some of that energy has been preserved as fossil energy, some is directly or indirectly usable; for example, via wind, hydro- or wave power.

Despite the fact that solar energy is the primary source of all forms of energy on the planet it is outside the scope of this work to explain or discuss how it can transform into the under-listed forms of energy reserve. Instead the worldwide reserve of energy as it affects modern civilization would be the major focus in the next sub-sections.

2.1.2 Worldwide Energy Reserve

2.1.2.1 Fossil fuels

The remaining reserves of fossil fuels are estimated as shown in Table 2.1.

Table 2.1: Fossil Energy Reserves

Fuel	Energy Reserves in ZJ
Coal	290.0
Oil	18.4
Gas	15.7

Source: http://en.wikipedia.org/wiki/World_energy_resources_and_consumption, 2010.

It has been reported that significant uncertainty exists for these figures due to the fact that the estimation of the remaining fuels on the planet depends largely on a detailed understanding of the Earth crust. This understanding is still less than perfect. For example, while modern drilling technology makes it possible to drill wells in up to 3 km of water to verify the exact composition of the geology, one half of the ocean is deeper than 3km, thereby leaving about a third of the planet beyond the reach of detailed analysis.

Coal

Coal is the most abundant fossil fuel. This was the fuel that launched the industrial revolution and has continued to grow in use. The major reserve geographical locations are as shown bold black spots in Figure 2.1. In essence most of the commercial coal deposits are located in places like India, China, Russia, Canada, Australia and USA. Coal is the fastest growing fossil fuel and its large reserves and global distribution would make it popular candidate to meet the energy demand of the global community, short of global warming concerns and other pollutants.



Source: http://www.mapsofworld.com, 2010

Figure 2.1: Geographical Distribution of Major Coal Deposits in the World

According to the International Energy Agency the proven reserves of coal are around 909 billion tones, which could sustain the current production rate for the next 155 years, although at 5% growth per annum this would be reduced to 40 years, or until 2051.

Oil

Oil reserves are the estimated quantities of crude oil that are claimed to be recoverable under existing economic and operating conditions. The total estimated amount of oil in an oil reservoir, including both producible and non-producible oil, is called *oil in place*. However, because of reservoir characteristics and limitations in petroleum extraction technologies only a fraction of this oil can be brought to the surface, and it is only this producible fraction that is considered to be *reserves*.

The total world oil reserves are as shown in Figure 2.2 and a simplified representation of the distribution is in Figure 2.3. Technically speaking, when petroleum occurs in a reservoir in a form that allows the crude material to be recovered by pumping operation as a free-flowing dark to light coloured liquid, it is often referred to as conventional petroleum or else unconventional.

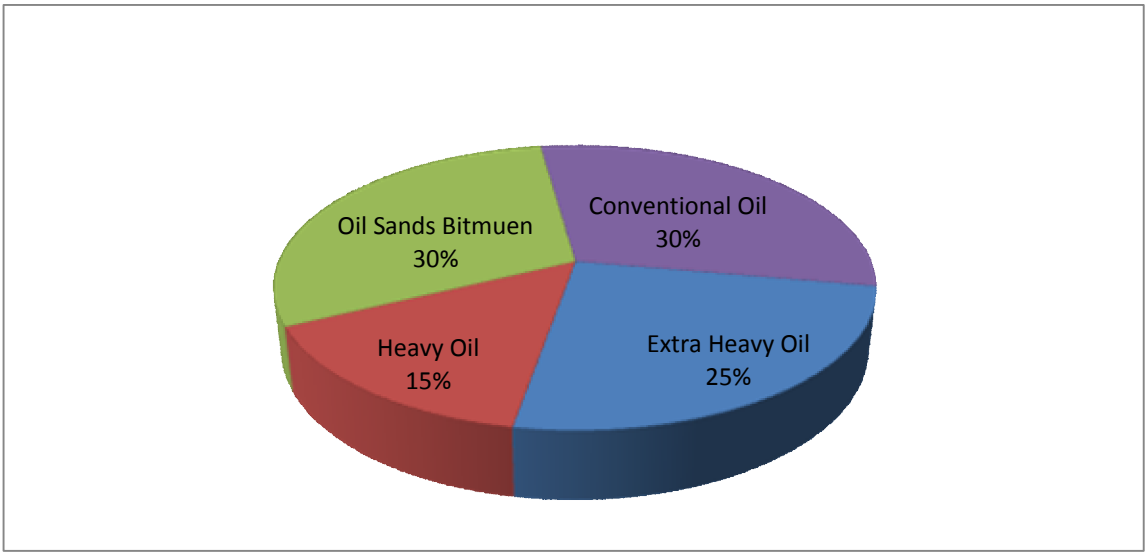


Figure 2.2: Total World Oil Reserves Source: http://en.wikipedia.org/wiki/oil_reserves , 2009

The major physical property that is today being used to differentiate between conventional and unconventional petroleum is their API gravity and the viscosity (see Figure 2.4).

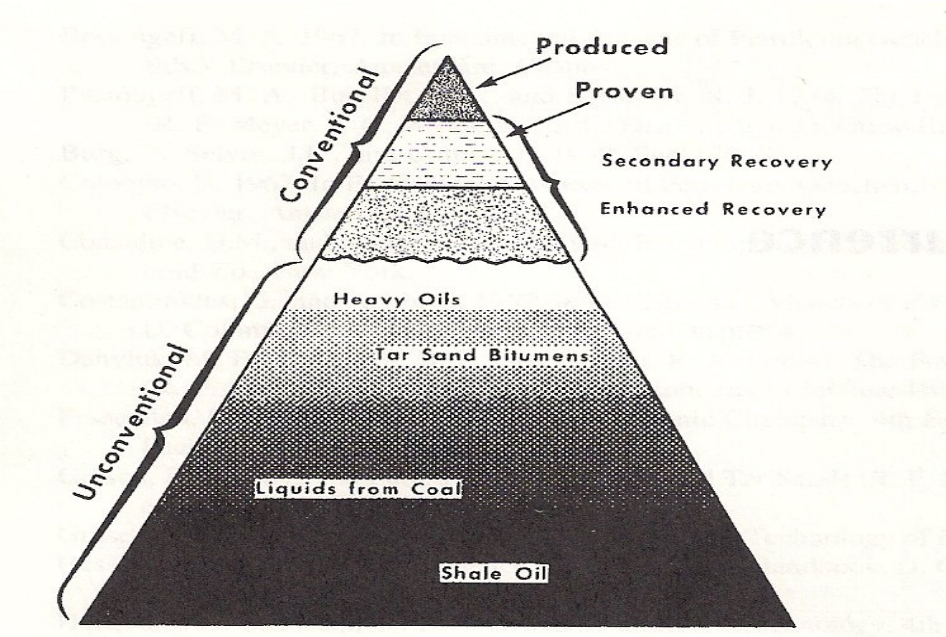


Figure 2.3: Simplified Representation of the Distribution of Fossil Fuel Liquids (Speight, 1999)

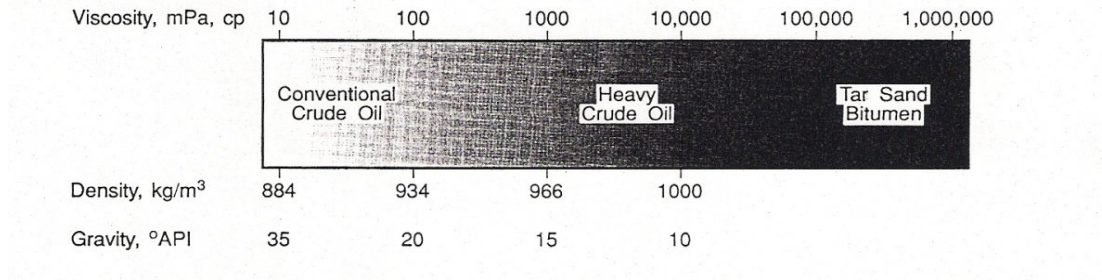
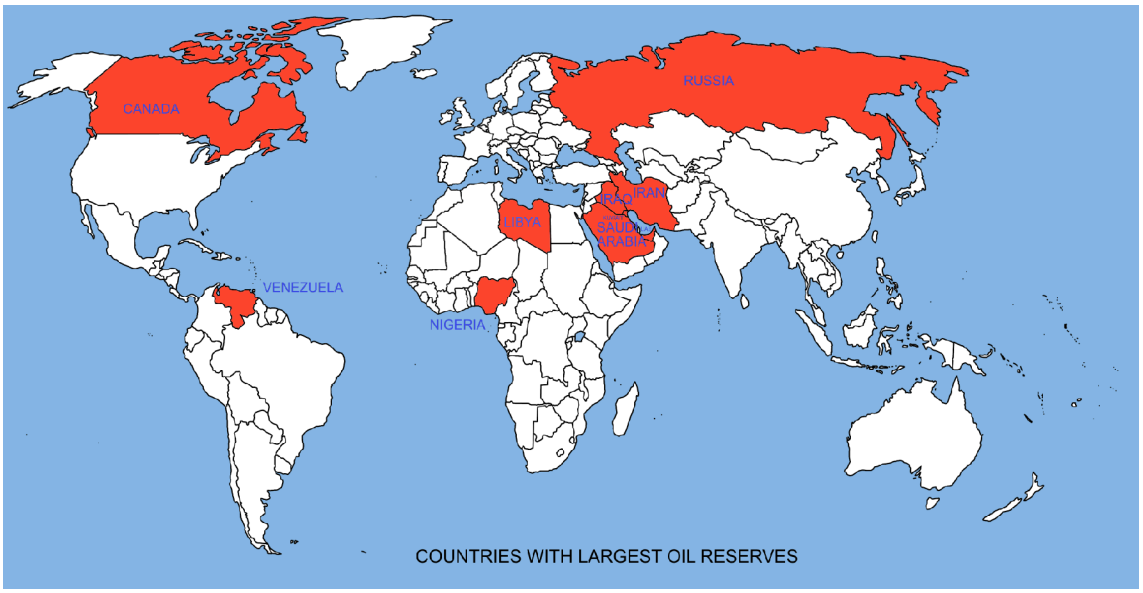


Figure 2.4: Classification of Fossil Fuel Liquids by Gravity-density

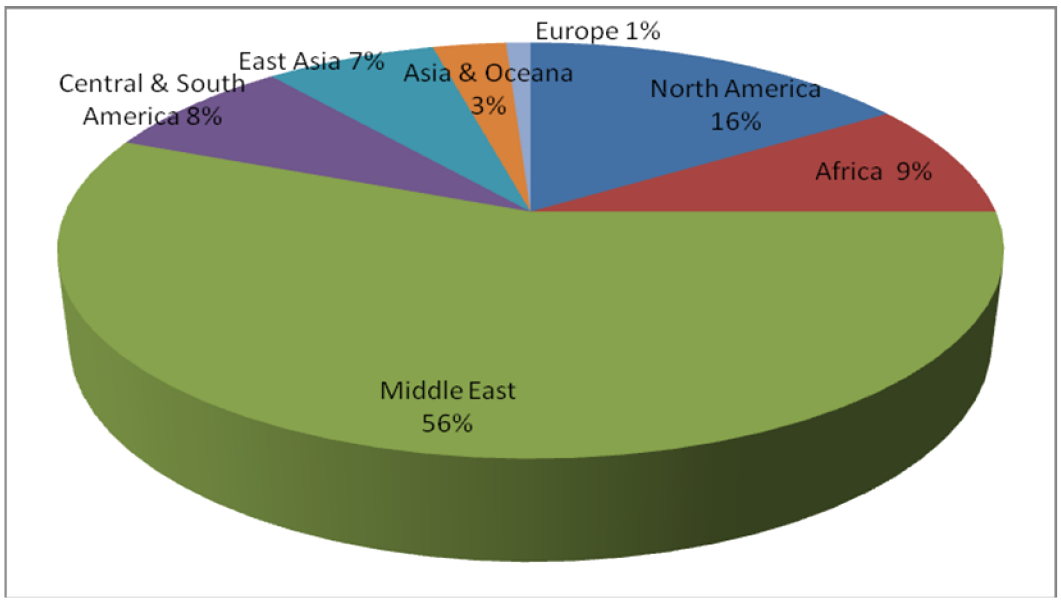
Conventional oil reserves

On a global and regional basis the reserves of conventional crude is shown in Figures 2.5 and 2.6



Source: http://en.wikipedia.org/wiki/oil_reserves,2009

Figure 2.5: Countries with Largest Oil Reserves in the World



Source: http://en.wikipedia.org/wiki/File:Remaining_oil.svg ,2010

Figure 2.6: World Oil Reserves on Regional Basis

Table 2.2: The Reserves of the First Major Seventeen Oil Producing Countries

Country	Reserves		Production		Reserve Life
	10^9bbl	10^9m^3	10^6bbl/day	10^3m^3/day	Years
Saudi Arabia	267	42.4	10.2	1,620	72
Canada	179	28.5	2.3	520	149
Iran	138	21.9	4.0	640	95
Iraq	115	18.3	2.1	330	150
Kuwait	104	16.5	2.6	410	110
United Arab Emirates	98	15.6	2.9	460	93
Venezuela	87	13.8	2.7	430	88
Russia	60	9.5	9.9	1,570	17
Libya	41	6.5	1.7	270	66
Nigeria	36	5.7	2.4	380	41
Kazakhstan	30	4.8	1.4	220	59
USA	21	3.3	7.5	1,190	8
China	16	2.5	3.9	620	11
Qatar	15	2.4	0.9	140	46
Algeria	12	1.9	2.2	350	15
Brazil	12	1.9	2.3	370	14
Mexico	12	1.9	3.5	560	9
Total of top seventeen reserves	1,243	197.6	63.5	10,100	54

Source: OPEC DATA, 2008

Unconventional reserves

There exists in petroleum accumulations that are pervasive throughout a large area. As shown above, examples include heavy crude oil, extra heavy oil, natural bitumen, and oil shale deposits. Their reserves are estimated thus:

Heavy Crude Oil Reserves: Heavy crude oils are the other types of petroleum that are different from conventional petroleum in so far as they are more difficult to recover from the subsurface reservoir. These materials have much more viscosity (i.e. lower APl gravity, say less than 25^o) than conventional petroleum, and primary recovery of these petroleum types usually requires thermal stimulation.

Information about their reserves is very scanty but however form parts of the petroleum business because of their fuel oil values and bitumen/ asphaltic contents.

Tar Sand Bitumen Reserves: In addition to conventional petroleum and heavy crude oils, there remains an even more viscous material that offers some relief to the potential shortfalls in supply; such material is the bitumen (extra heavy oil) found in tar sand (oil sand) deposits. Their APl gravity is normally less than 10.

Tar sand deposits are widely distributed throughout the world. The potential reserves of bitumen that occur in tar sand deposits have been variously estimated on a worldwide basis as being in excess of 3 trillion barrels of petroleum equivalent.

Shale Reserves: A special class of bituminous rock that has achieved some level of importance is the so-called oil shales. These are the argillaceous, laminated sediments of generally high organic content that can be thermally decomposed to yield appreciable amounts of oil commonly referred to as shale oil.

Very little is known about it's world deposits and reserve. However, as at 1983, its world reserve was estimated to be 15.30 gigatons (a gigaton = one billion barrel).

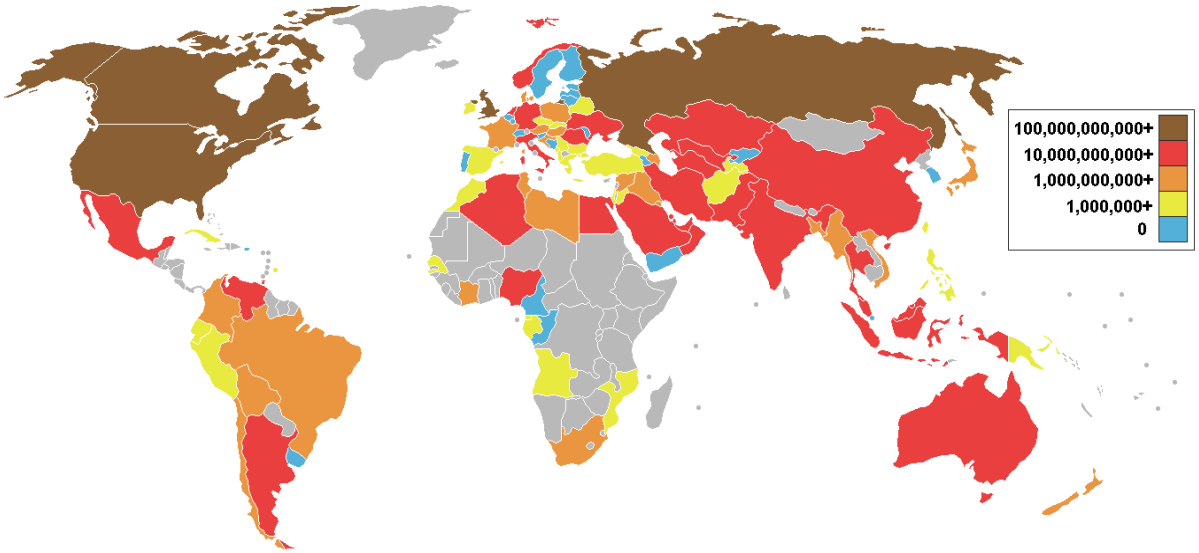
Natural Gas Reserves: Natural gas is a gas consisting primarily of methane. It is found associated with other fossil fuels, in coal beds, as methane clathrates, and is created by methanogenic organisms in marshes, bogs, and landfills. It is an important fuel source, a major feedstock for fertilizers, and a potent greenhouse gas.

Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane. The by-products of that processing include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, elemental sulfur, carbon dioxide, water vapor and sometimes helium and nitrogen.

Natural gas is often informally referred to as simply gas, especially when compared to other energy sources such as oil or coal.

Fossil natural gas can be "associated" (found in oil fields) or "non-associated" (isolated in natural gas fields), and is also found in coal beds (as coalbed methane). Natural gas is commercially produced from oil fields and natural gas fields. Gas produced from oil wells is called casinghead gas or associated gas. The natural gas industry is producing gas from increasingly more challenging resource types: sour gas, tight gas, shale gas and coalbed methane.

The reserves and the global deposits are as shown in Figure 2.7. The world's largest proven gas reserves (wikipedia.org/wiki/natural_gas#cite_note-2, 2010) are located in Russia, with 4.757×10^{13} m³ (1.6×10^{15} cu ft). Russia is also the world's largest natural gas producer, through the Gazprom Company. Major proven resources (with year of estimate) (in billion cubic metres) are world 175,400 (2006), Russia 47,570 (2006), Iran 26,370 (2006), Qatar 25,790 (2007), Saudi Arabia 6,568 (2006) and United Arab Emirates 5,823 (2006).



Source: http://www.nat_gas_htm.,2009

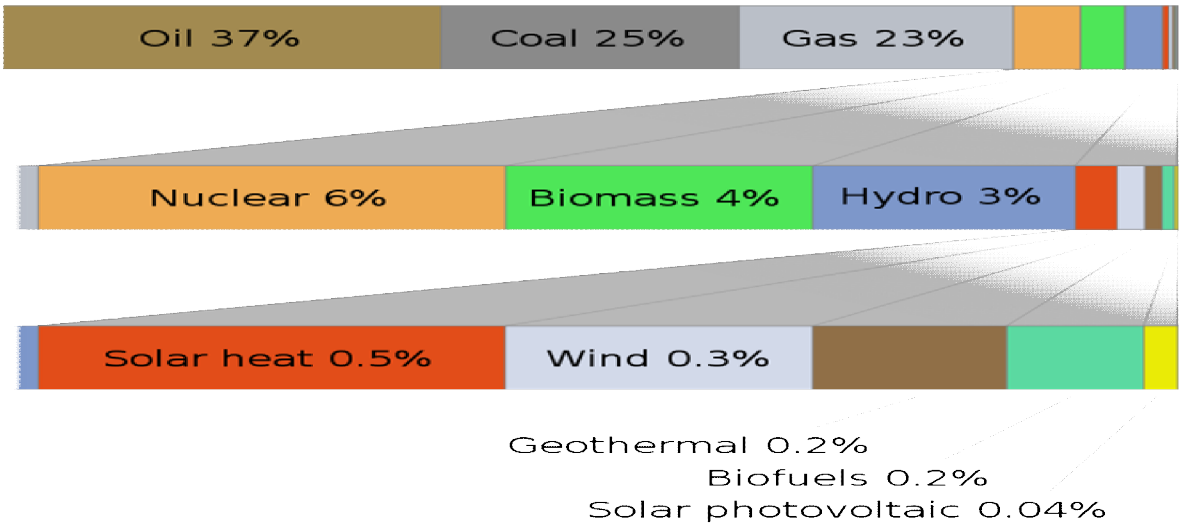
Figure 2.7: Worldwide Reserves and Deposit of Natural Gas

2.1.2.2 Other Sources of Energy

The author realizes the importance and needs of detailed discussion of other sources of energy such as nuclear fission and fusion as well as renewables (solar, wind, wave, tidal, geothermal and biomass) in this work but for lack of space and within the limit of the scope. Therefore interested readers are hereby referred to http://en.wikipedia.org/wiki/File:2004_Worldwide_Energy_Sources_graph.png, 2010.

2.1.3 World Energy Consumption

The world energy consumption pattern is as shown in a chart presented as Figure 2.8.



Source: http://en.wikipedia.org/wiki/File:World_energy_usage_width_chart.svg ,2010

Figure 2.8: Consumption Pattern of Energy from Various Sources

The United States energy Information Administration regularly publishes a report on world energy consumption for most types of primary energy resources. This is as presented in Table 2.3.

Table 2.3: Statistical Data of Worldwide Consumption of Various Energy Sources

Fuel type	**Average power in TW**		
	1980	**2004**	**2006**
Oil	4.38	5.58	5.74
Gas	1.80	3.45	3.61
Coal	2.34	3.87	4.27
Hydroelectric	0.599	0.933	0.995
Nuclear power	0.253	0.914	0.929
Solar energy, wood	-	-	-
Total	**9.48**	**15.0**	**15.8**

Source: http://en.wikipedia.org/wiki/File:World_energy_usage_width_chart.svg ,2010

2.1.3.1 Primary energy consumption

Fossil Fuel Consumption

The twentieth century saw a rapid twentyfold increase in the use of fossil fuels. Between 1980 and 2006, the worldwide annual growth rate was 20%. According to the US Energy Information Administration's 2006 estimate, the estimated 471.8 EJ total consumption in 2004 fossil fuels supply 86% of the world's energy.

Coal fueled the industrial revolution in the 18th and 19th century. With the advent of the automobile, airplanes and the spreading use of electricity, oil became the dominant fuel during the twentieth century. The growth of oil as the largest fossil fuel was further enabled by steadily dropping prices from 1920 until 1973. After the oil shocks of 1973 and 1979, during which the price of oil increased from 5 to 45 US dollars per barrel, there was a shift away from oi1. Coal, natural gas, and nuclear became the fuels of choice for electricity generation and conservation

measures increased energy efficiency. In the U.S. the average car more than doubled the number of miles per gallon. Japan, which bore the brunt of the oil shocks had made spectacular improvements and now has the highest energy efficiency in the world. From 1965 to 2008, the use of fossil fuels has continued to grow and their share of the energy supply has increased. From 2003 to 2008, coal, which is one of the dirtiest sources of energy, was the fastest growing fossil fuel.

Nuclear Power Consumption

In 2005 nuclear power accounted for 6.3% of world's total primary energy supply. The nuclear power production in 2006 accounted for 2,658 TWh (23.3 EJ), which was 16% of world's total electricity production. In November 2007, there were 439 operational nuclear reactors worldwide, with total capacity of 372,002 MWe. A further 33 reactors were under construction, 94 reactors were planned and 222 reactors were proposed.

2.1.3.2 Renewable energy Consumption

In 2004, renewable energy supplied around 7% of the world's energy consumption. The renewables sector has been growing significantly since the last years of the 20th century, and in 2005 the total new investment was estimated to have been 38 billion US dollars. Germany and China lead with investments of about 7 billion US dollars each, followed by the United States, Spain, Japan, and India. This resulted in an additional 35 GW of capacity during the year.

Within the scope of this work and preferably due to lack of space detailed report on renewable energy sources of consumption such as hydropower, biomass and biofuels, bioethanol, wind power, solar power, etc, interested readers are herby referred to (http://en.wikipedia.org/wiki/File:World_energy_usage_width_chart.svg ,2010).

By country

Energy by country and List of countries by energy consumption per capita Energy consumption is loosely correlated with gross national product and climate, but there is a large difference even between the most highly developed countries, such as Japan and Germany with 6 kW per person and United States with 11.4 kW per person. In developing countries particularly those which are sub-tropical or tropical such as India the per person energy use is closer to 0.7 kW. Bangladesh has the lowest consumption with 0.2 kW per person.

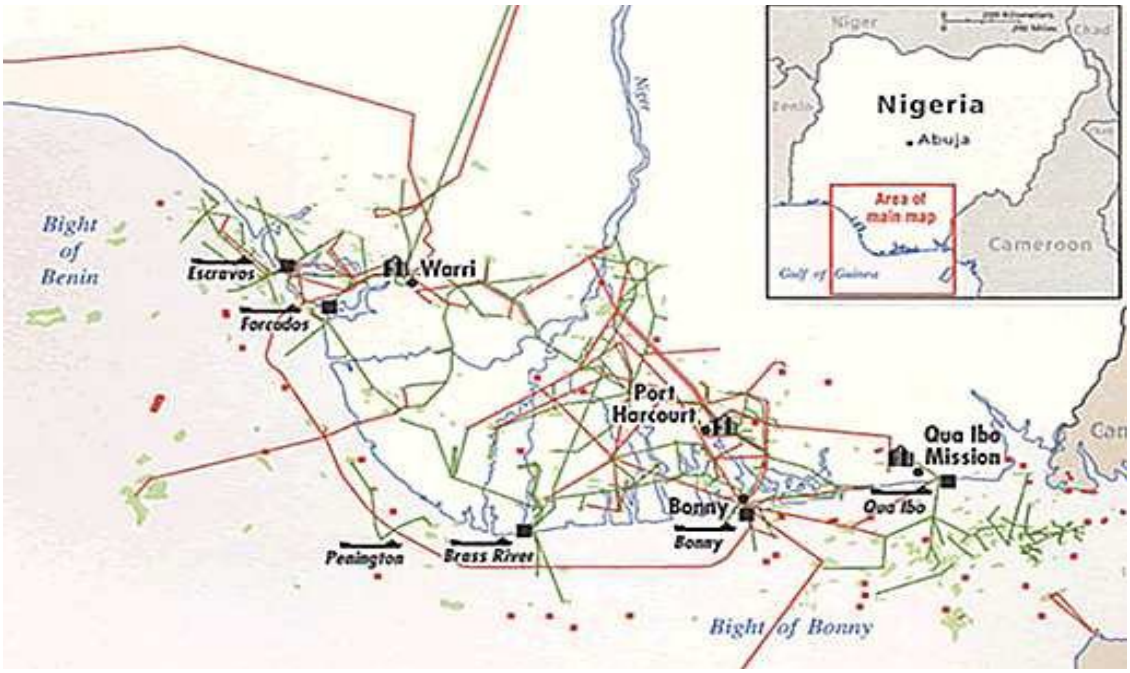
By sector

Industrial users (agriculture, mining, manufacturing, and construction) consume about 37% of the total 15 TW. Personal and commercial transportation consumes 20%; residential heating, lighting, and appliances use 11%; and commercial uses (lighting, heating and cooling of commercial buildings, and provision of water and sewer services) amount to 5% of the total.

The other 27% of the world's energy is lost in energy transmission and generation. In 2005, global electricity consumption averaged 2 TW. The energy rate used to generate 2 TW of electricity is approximately 5 TW, as the efficiency of a typical existing power plant is around 40%. The new generation of gas-fired plants reaches a substantially higher efficiency of 55%.

2.2 NIGERIA ENERGY PROFILE

The Nigerian economy is heavily dependent on the oil sector which, according to the International Monetary Fund (IMF Report, 2009), accounts for over 95 percent of export earnings and about 65 percent of government revenues. The oil industry is primarily located in the Niger Delta as shown in Figure 2.9. In addition to oil, Nigeria holds the largest natural gas reserves in Africa.



Source: Nigeria Energy Data, Statistics and Analysis - Oil, Gas, Electricity, Coal-(October, 2010) file:///Z:/NewCABs/V6/Nigeria/Full.html

Figure 2.9: Map of Niger Delta Region of Nigeria

2.2.1 Nigeria Energy Reserve

2.2.1.1 Crude oil

According to the *O*il and Gas Journal (http://www.eia.doe.gov, 2011), Nigeria had an estimated 37.2 billion barrels of proven oil reserves as of January 2010. The majority of reserves are found along the country's Niger River Delta and offshore in the Bight of Benin, the Gulf of Guinea and the light of Bonny as shown in Figure 2.9. Current exploration activities are mostly focused in the deep and ultra-deep offshore with some activities in the Chad basin, located in the northeast of the country.

According to the Energy Intelligence Group's International Crude Oil Market Handbook, Nigeria's export blends are light, sweet crudes, with gravities ranging from API 29 – 47 degrees and low sulfur contents of 0.05 – 0.3 percent. Most Nigerian crudes trade at a premium to Brent, the North Sea benchmark crude.

2.2.1.2 Natural Gas

Nigeria had 185 trillion cubic feet (Tcf) of proven natural gas reserves as of January 2010, which makes Nigeria the eighth largest natural gas reserve holder in the world and the largest in Africa (http://www.ngex.com/business/public/newsinfo.php, 2011). In 2008, Nigeria produced about 1,400 Bcf of marketed natural gas, ranking the country as 23rd in the world (gross production was 2,600 Bcf). The majority of the natural gas reserves are also located in the Niger Delta.

2.2.1.3 Coal

According to *World Energy Council*, Nigeria's reserve of recoverable coal is estimated at about 210 million short tons.

Nigeria's Other Forms of Energy

Statistical data on the reserve or estimation of other forms of energy is very scanty and in some cases not available for any meaningful economic projection. On that account, the discussion of Nigeria energy profile will to a large extent be limited to the ones mentioned above.

2.2.2 Nigeria's Energy Production and Consumption

In summary, the overview of Nigeria's pattern of Energy Production and Consumption is as shown in Table 2.4.

Table 2.4: Overview of Energy Production and Consumption in Nigeria

Energy Description	Estimation
Oil Production (2009)	2.21 million bbl/ day, of which 1.8 million bbl was crude oil
Oil Consumption (2009)	280 thousand bbl/day
Crude Oil Refining Capacity (2010)	505 thousand bbl/day
Major Refineries	Port Harcourt-Rivers State (150,000), Kaduna (110,000), Warri (125,000), Port Harcourt-Alesa Eleme (120,000),
Natural Gas Production (2008)	1,159 billion cubic feet
Natural Gas Consumption (2008)	432 billion cubic feet
Coal Production (2008)	0.009 million short tons
Coal Consumption (2008)	0.012 million short tons
Electricity Installed Capacity (2007E)	5.898 gigawatts
Total Energy Consumption (2007E)	4 quadrillion Btus*, of which Combustible Renewables and Waste (80.2%), Natural Gas (9.9%), Oil (9.4%), Hydroelectricity (0.5%), Coal (0%), Nuclear (0%) (IEA data)

Source: Nigeria Energy Data, Statistics and Analysis - Oil, Gas, Electricity, Coal-(October, 2010) file:///Z:/NewCABs/V6/Nigeria/Full.html

* The total energy consumption statistic includes petroleum, dry natural gas, coal, net hydro, nuclear, geothermal, solar, wind, wood and waste electric power.

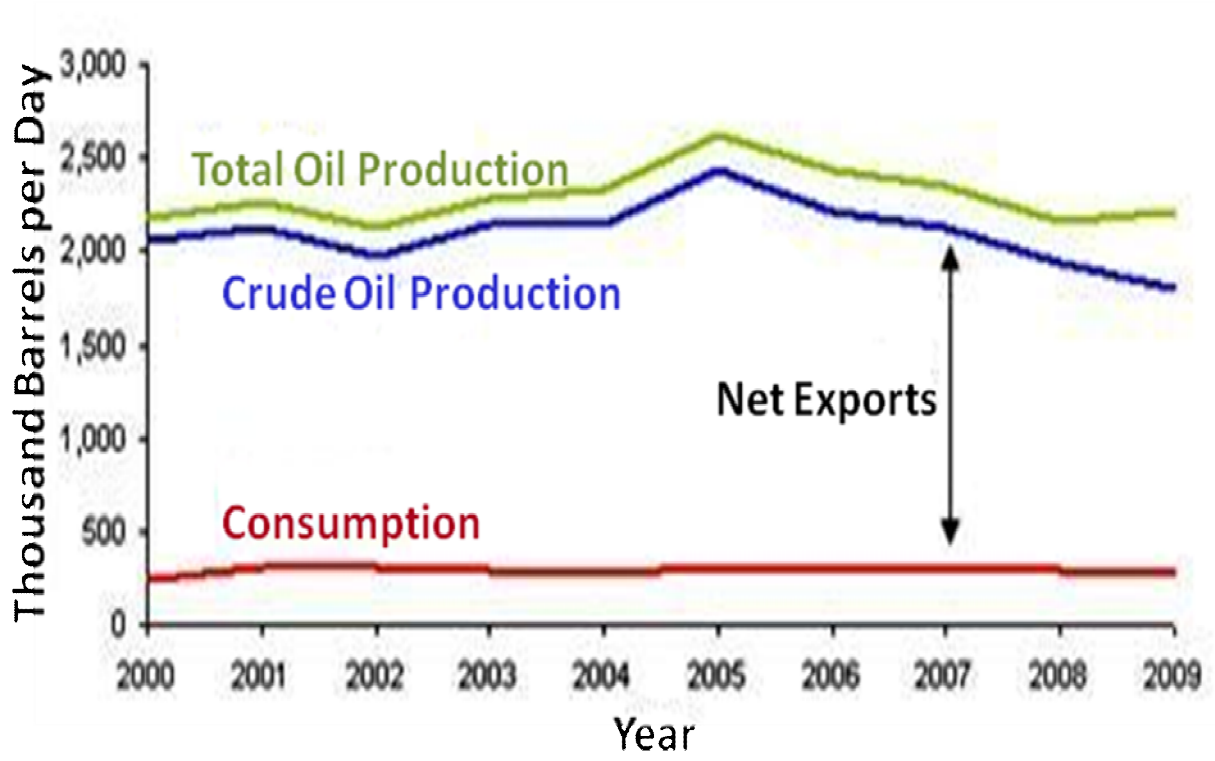


Figure 2.10: Nigeria's Oil Production and Consumption Source: http://www.eia.doe.gov, 2011

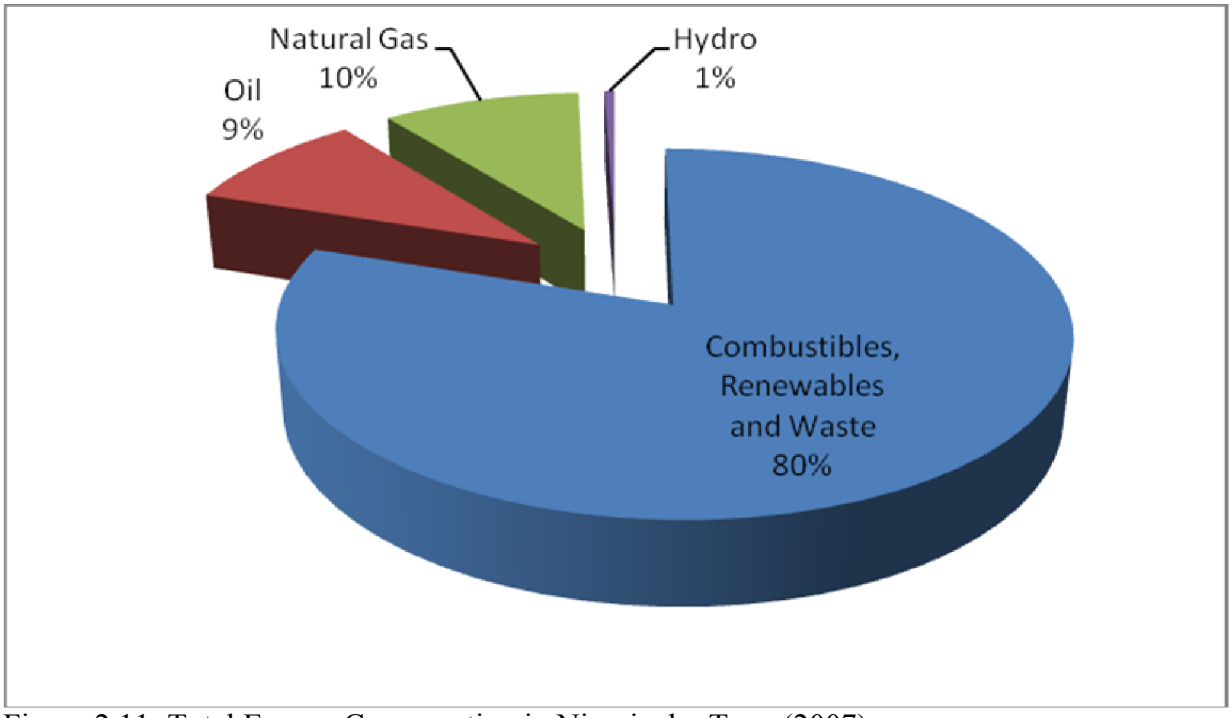
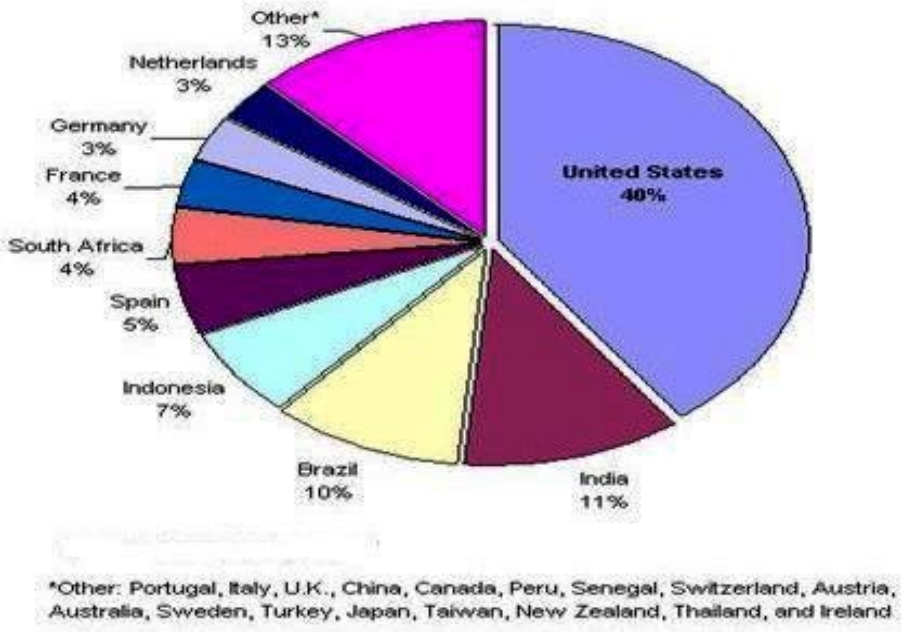


Figure 2.11: Total Energy Consumption in Nigeria, by Type (2007)
Source: http://www.eia.doe.gov, 2011

2.2.2.1 Nigeria's Crude Oil Exports

In 2009, Nigeria exported most of its 2.2 million bbl/d of total oil production (approximately 1.9million bbl/d were exported). Of this, close to 800,000bbl/d (40 percent) was exported to the United States.

Additional importers of Nigerian crude oil include Europe (24 percent), Asia (20%), Brazil (10%), and South Africa (4%). Despite shut-in production, Nigerian trade patterns appear to have remained stable over the past year, most of which can be attributed to capacity additions combined with slightly decreasing domestic consumption and declining world demand. Figure 2.12 represents the chart on how Nigeria's oil export is distributed worldwide as at 2009.



Source: Global Trade Atlas, EIA, APEX

Figure 2.12: Nigerian Oil Exports by Country in 2009.

2.2.2.2 Nigeria's Gas Exports

A significant portion of Nigeria's natural gas is processed into LNG. In 2009, Nigeria exported close to 500 Bcf of LNG. Of this, 13.3 Bcf went to the United States, providing 3 percent of total U.S. LNG imports (2 percent of Nigerian exports). Most of Nigeria's LNG was

exported to Europe (66 percent), mainly Spain (31 percent), France (15 percent) and Portugal (13 percent). Other export destinations include Asia (15 percent) and Mexico (16 percent). Nigerian LNG Exports were down close to 30 percent from 2008 volumes which can also be attributable to problems in the Niger Delta, specifically problems at the Soku gas processing facility.

Nigeria's main natural gas project is the Nigeria Liquefied Natural Gas (NLNG) facility on Bonny Island. Partners including NNPC, Shell, Total and Agip completed the first phase of the facility in September 1999. NLNG currently has six trains and a production capacity of 22 million tons per year (1.1 trillion cubic feet). A seventh train is under construction but this addition has been delayed until 2012.

Three additional LNG plants with a total of seven trains are expected to come online after 2012, these include OK LNG (4 trains), Brass LNG (2 trains), and Progress LNG (1 train).

2.3 THE SIGNIFICANCE OF PETROLEUM COMPARED WITH OTHER SOURCES OF ENERGY

The twentieth century and beyond might be described as pre-eminently the age of petroleum. Although, oil was first commercially exploited in any scale in the later nineteenth century, the 20th century has seen the development of oil into "the biggest business in the world''.

2.3.1 Factors Responsible for the Growth of Oil and Gas Industries

Strictly speaking, customer demand has propelled the growth. This can be attributed to the following factors:

- Versatility for the manufacture of a very wide range of products.
- Convenience and cleanliness while in use

- Ease of transportation and storage
- Efficiency in their places of application especially as fuels for engines
- Raw materials for lubricants and feedstock for petrochemicals

These factors have powerfully stimulated growth and given petroleum major importance in the economies of producer and consumer communities alike.

At this juncture, because of the bearing role that engine oil has played in this research work, it is hereby discussed in the following section.

2.4 ENGINE OILS PROFILE

After kerosene the early petroleum refiners wanted paraffin wax for the manufacture of candles, and lubricating oils were at first byproducts of paraffin wax manufacturing. The preferred lubricants in the 1860's were lard oil, sperm oil, and tallow. The demand that existed for kerosene did not develop for petroleum-derived lubricating oils. In fact, oils were used to supplement the animal and vegetable oils as lubricants. However, as the trend to heavier industry increased, the demand for mineral lubricating oils increased and after the 1890s petroleum displaced animal and vegetable oils as the source of lubricants for most purposes.

2.4.1 Composition

Lubricating oils are distinguished from other fractions of crude oil by their usually high (>400^{o}C) boiling point, as well as their high viscosity. Materials suitable for the production of lubricating oils are comprised principally of hydrocarbons containing from 25 to 35 or even 40 carbon atoms per molecule, whereas residual stocks may contain hydrocarbons with 50-60 or more (up to 80 or so) carbon atoms per molecule. The composition of lubricating oil may be substantially different from the lubricant fraction from which it is derived, since wax (normal

paraffins) is removed by distillation or refining by solvent extraction and adsorption preferentially removes nonhydrocarbon constituents as well as poly-nuclear aromatic compounds and the condensed cycloparaffins.

Nevertheless, there are general indications that the lubricant fraction contains a greater proportion of normal and branched paraffins than the lower boiling portions of petroleum. For the polycycloparaffins, a good proportion of the rings appear to be in condensed structures, and both cyclopentyl and cyclohexyl nuclei are present. The methylene groups appear principally in unsubstituted chains at least four carbon atoms in length, but the cycloparaffin rings are highly substituted with relatively short side chains.

Mono-, di- and trinuclear aromatic compounds appear to be the main constituents of the aromatic portion, but material with aromatic nuclei per molecule may also be present. For the dinuclear aromatics, most of the material consists of naphthalene types. For the trinuclear aromatics, the phenanthrene type of structure predominates over the anthracene type. There are also indications that the greater part of the aromatic compounds occurs as mixed aromatic-cycloparaffin compounds.

Although structural determinations allow the development of general rules about the structural entities in petroleum, there are nevertheless variations in the composition of petroleum fractions from different sources, and care must be taken to avoid a too literal interpretation of the derived data.

2.4.2 Manufacture

The production of lubricating oils is well established and usually consists of four basic procedures:

1. Distillation and deasphalting to remove the heavier constituents of the feedstock.

2. Solvent refining and/or hydrogen treatment to remove the nonhydrocarbon constituents and to improve the feedstock quality.
3. Dewaxing to remove the wax constituents and to improve the low-temperature properties.
4. Clay treatment or hydrogen treatment to prevent instability of the product.
5. Additives to improve the quality and enhancement of application.

2.4.3 Properties and Uses

Lubricating oils may be divided into many categories according to the service they are intended to perform. However, there are two main groups: (1) oils used in intermittent service, such as motor and aviation oils, and (2) oils designed for continuous service, such as turbine oils. Lubricating oil is distinguished from other fractions of crude oil by a high boiling point as earlier stated, as well as high viscosity. In fact, lubricating oil is classified on the basis of viscosity of Table 2.5.

Table 2.5: Viscosity of Various Lubricating Oil Grades (Speight, 1999)

Lubricants type	Kinematic viscosity, Cst @ 100^{o}C		Dynamic viscosity, cP
	Minimum	Maximum	Maximum
SAE 10W	4.1	N/A	3500 @ -20
SAE 15W	5.6	N/A	3500 @ -15
SAE 20W	5.6	N/A	4500 @ -10
SAE 25W	9.3	N/A	6000 @ -5
SAE 20	5.6	5.6	N/A
SAE 30	9.3	12.5	N/A
SAE 40	12.5	16.3	N/A
SAE 50	16.3	21.9	N/A

This classification is based on the SAE (Society of Automotive Engineers) and J 300 specification. The single grade oils (e.g., SAE 20, etc.) correspond to a single class and have to be selected according to engine manufacturer specifications, and climatic conditions. At -20^{o}C, multi-grade lubricating oil such as SAE 10W-30 possesses the viscosity of a SAE 30 oil.

Oils used in intermittent service must show the least possible change in viscosity with temperature; that is, their viscosity indices must be high. These oils must be changed at frequent intervals to remove the foreign matter collected during service. The stability of such oils is of less importance than the stability of oils used in continuous service for prolonged periods without renewal.

Oils used in continuous service must be extremely stable, but their viscosity indices may be low because the engines operate at fairly constant temperature without frequent shutdown.

2.4.4 Other Oil Products

Lubricating oils are not the only materials manufactured from the high-boiling fraction of petroleum, and there are several important types of oil that may be contained in the lubricant fraction. Among them are:

a. White oils for cosmetics, textile lubrication, insecticide vehicles, paper impregnation, laxatives, etc.

b. Insulating oils that are employed in transformers, circuit breakers for insulating purpose.

c. Insecticides that are usually used as carriers for active poisons, as in the household and livestock sprays.

Within the scope of this work used oils that fall into the categories of intermittent usage was of concern.

2.4.5 Lubricating Oil Additives

Quite often lubricating oils, even when produced with the use of the most up-to-date refining methods, do not completely comply with customer's demand specifications. However, the required service properties can be ensured by incorporating various additives into the base oil.

Normally the following types of additives are used for upgrading lubricants: antioxidant, anticorrosion, depressants (pour-point lower), viscous enhancer, anti-wear, detergency (i.e, anti-sludge), antifoam, and multifunctional ones.

The major concern is that some of these additives are detrimental to human health especially when improperly discharged in an incorporated form with used oil into the environment. In fact it is reported that some of them are cancerous (Mohammed *et al*, 2004).

2.4.6 Deterioration of Oil in Use

Lubricating oil in the engine deteriorates in two ways: it undergoes chemical and physical changes due mainly to oxidation and it becomes contaminated by material from the combustion chamber, its own degradation products and airborne dust (Anonymous, 1983). Although physical contaminants can be removed by a filter which is fitted to all engine, acidic product of combustion are normally countered by the alkalinity in the oil. Contamination of the oil from the unburnt fuel and water of combustion, although a problem in the past, is of less importance nowadays due to improved thermostating of the engines, always provided that the engine is properly maintained.

Soot is formed as a result of imperfect combustion such as when idling or running under rich mixture conditions. Most of this is blown out by exhaust, but some contaminates the oil on the pistons and cylinders and then drains down to the crank case. In gasoline engines, lead

compounds are produced from the fuel additives and pass into the oil with soot. These solid contaminants, in conjunction with oil and water, may form a sludge that is essentially an emulsion of water in oil stabilized by the solids. This sludge may settle out in the crankcase or be circulated with the oil and block the oil ways. Oil filters are incorporated in the oil circulation system to remove these contaminants as far as possible, as well as any airborne dust that escapes the air filter and the air intake system. However, there is limit to what the oil filter can remove, and it too may be blocked if sludge has become excessive. The conditions under which oil is used in an engine are very conducive to oxidation. Oil mist is in intimate contact with air at fairly high temperature in the crankcase and at even higher temperatures in the combustion chamber. Oil films are subjected to high temperatures on the cylinder walls, the pistons, and piston rings. Oxidation products are formed, their nature depending largely on the temperature. In the crankcase, acidic materials and complex carbonaceous products known as asphalthenes are produced and, in association with the fuel contaminants already mentioned, help to form a stable sludge that is characteristic of low temperature operation. In the combustion chamber and around the piston rings, the oil forms deposits of ‘’carbon’’ by a combination of oxidation and thermal degradation. Part of this deposit is washed back to the sump and part remains in the combustion space on the piston head and in the ring grooves. All these effect of oxidation aggravate the contamination of the oil beyond that resulting from the fuel. Although, the presence of anti-oxidant additives retard the occurrence of oxidation and also prevents the oil from becoming acidic, when it would corrode bearing materials such as copper/lead, there is still a limit anti-oxidant can do in the deterioration.

On the average, the hydrocarbon composition of used engine oil is as shown in Table 2.6.

Table 2.6: Typical Composition of Used Engine Oil (Vazquez-Duhalt, 1989)

Constituents	Concentration, % wt.
Aliphatic Hydrocarbon	73-80
Monoaromatic Hydrocarbon	11-15
Diaromatic Hydrocarbon	2-5
Polyaromatic Hydrocarbon	4-8

It has to be stated that based on the Table 2.6, the aliphatic content is very high and on that basis, the used engine oil will be effective in peptizing or solublizing the asphalthene, thereby availing it for easy thermal decomposition, which ultimately will result into the enhancement of light-ends as reflected in the title of the research.

2.4.7 Regeneration/Recovery of Used Engine Oils

Because of the negative effects of used oil on human health and environment and the demand for sustainable development of our natural resources (Evdokimov and Fooks, 1989), in most industrially developed and developing countries, UEO legislation on collection centers, processing, regenerations have already gained popularity. Some of the multinational private and public companies and firms that are involved in UEO regeneration and/or recovery are: Sinohio-Canada, Recyclon- Sweden, ENTRA and Meinken - Germany, Matthys/Garap and Regelub - France, UOP, PROP, KTI and Lyondell Petrochemical Company - United States of America, Vtornefteprodukt- Russia, Rotovac- Finland, MOR- United Kingdom, Lubrex and Luwa-Switzerland, etc.

All these companies mentioned above reprocess used oils on the following technological bases:

(a) Partial Chemical Regeneration: This is explained by the fact that the UEO had had to undergo some forms of chemical transformation (Evdokimov and Fooks, 1989) before the base oil would be recovered. This is as shown in the Figure 2.13:

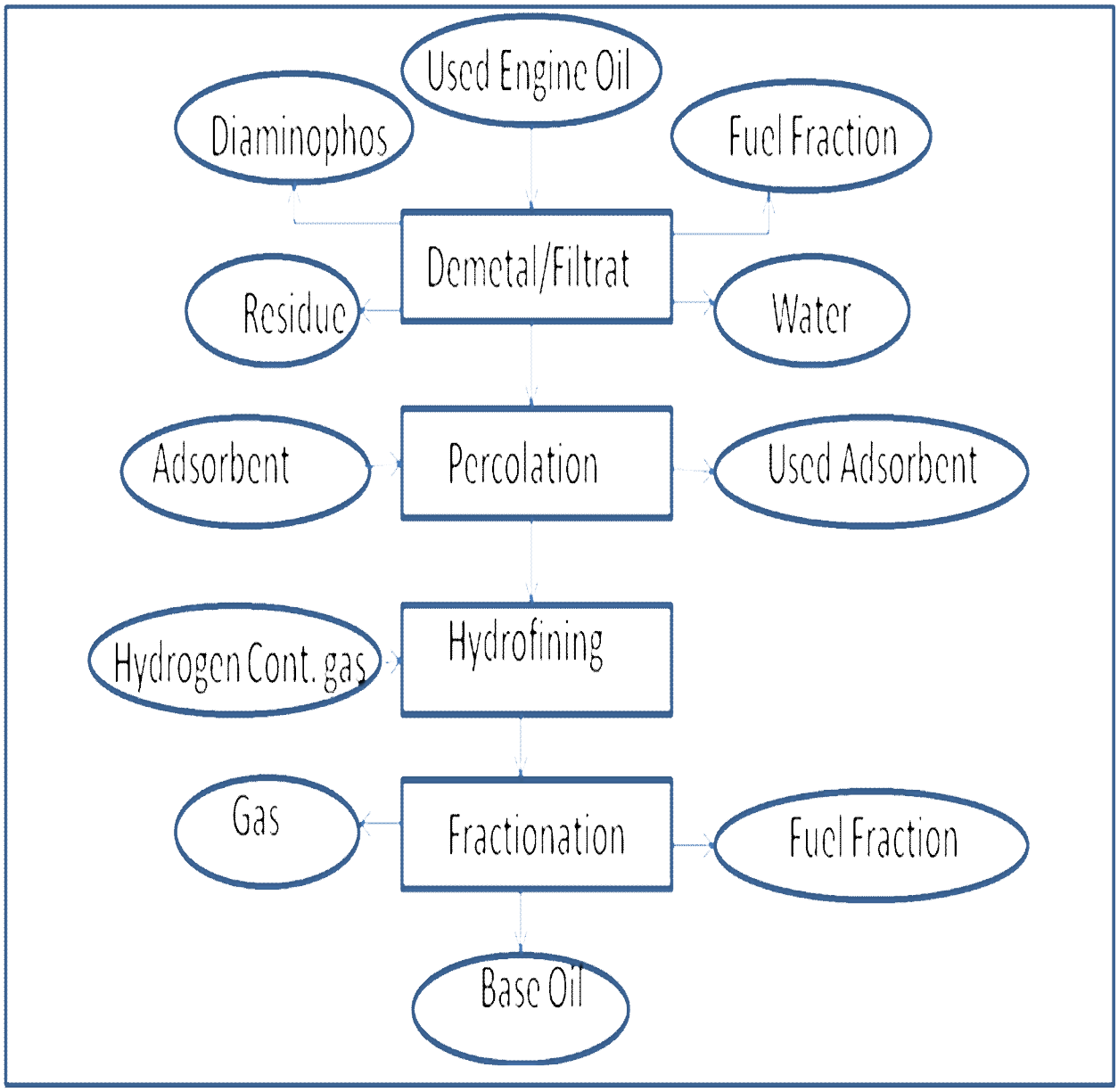


Figure 2.13: Partial Regeneration Method of Used Engine Oil

(b) Physical Regeneration: In this case, no form of chemical transformation is associated with the regeneration process. The major aim is to reduce/remove dirts and impurities that are present in the used engine oil. This is shown in Figure 2.14.

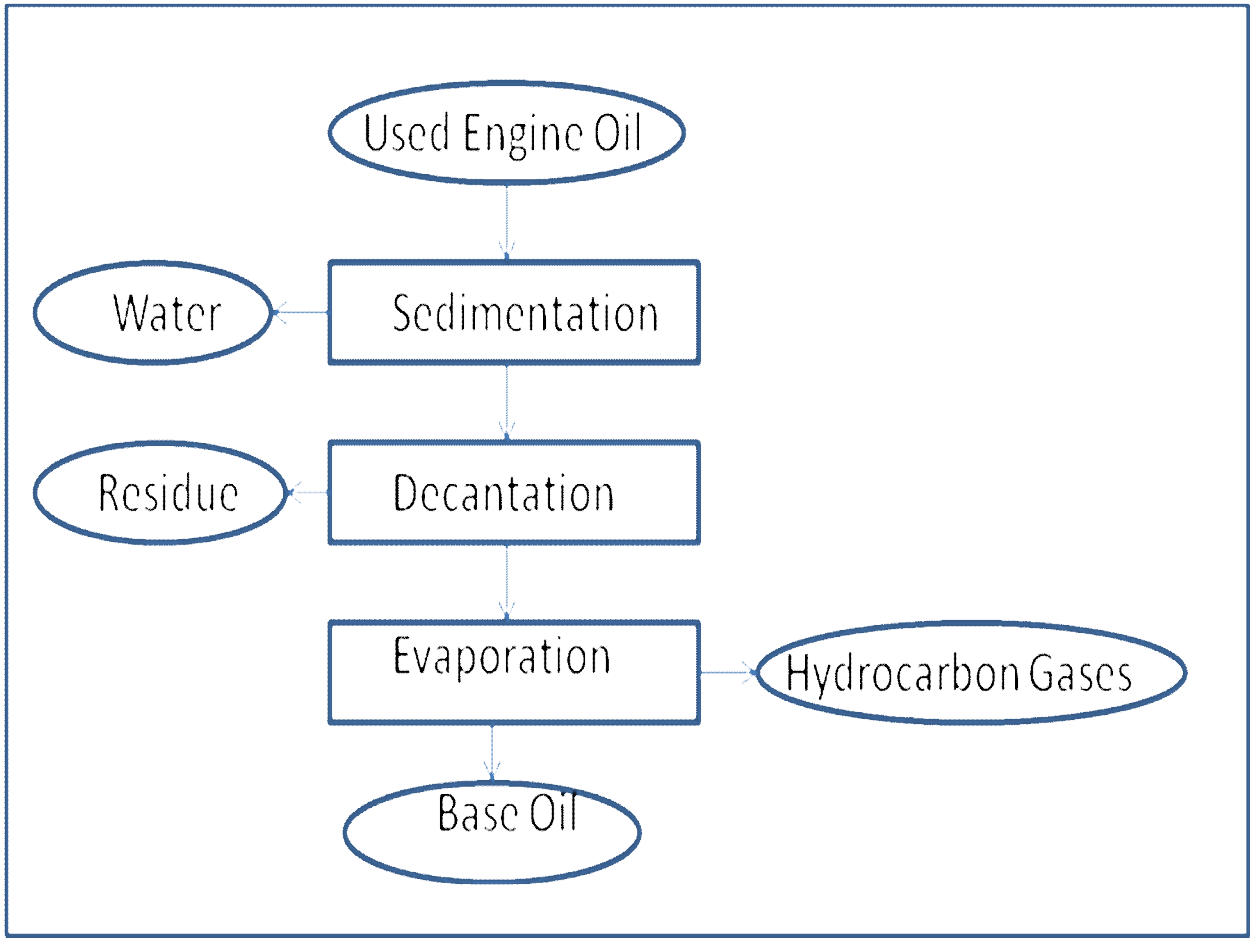


Figure 2.14: Typical Physical Regeneration Method of Used Engine Oil

It is this method that would be employed in this research work.

(c) Total Chemical Transformation Regeneration: In this process, UEO is totally chemically transformed into new products so that fuel oil and gasoline are the major products that shall be favorably produced.

2.5 CRUDE AND LUBRICATING OILS FOR SUSTAINABLE DEVELOPMENT

The challenge that mankind is being confronted with is that petroleum as the most reliable source of energy, which has accumulated over geological age is being consumed at a rate more than million times faster than they are formed. The resultant effect is the uncontrollable hike in price because of high demand, high cost of processing as a result of low API gravity of many crude feeds that are becoming available to refineries and above all, fast depleting rate of reserves (Bhaskara Rao, 1990; Swain, 1997). Khan and Patmore (1997) reported that one of the essential steps that is required of refineries therefore, is the upgrading of heavy feedstocks in order to complement the reserve of the light crudes. In another development, there is the need for stringent controls over the amounts and types of emissions from the use of petroleum and its products.

The challenge is for the development of technological concepts that will provide the maximum recovery of energy from petroleum not only cheaply but also efficiently and with minimal detriment to the environment.

2.6 PETROLEUM WITHIN THE CONTEXT OF THIS WORK

All over the world, at various depths beneath land and sea, there are accumulations of hydrocarbons formed long ago by decomposition of animal and vegetable remains. Hydrocarbons are compounds of hydrogen and carbon which, at normal temperatures and pressures, may be gaseous, liquid or solid according to the complexity of their molecules. The natural deposits are correspondingly gaseous, liquid or solid, depending on the relative proportion of the various hydrocarbons present in the mixture.

In its widest sense, petroleum embraces all hydrocarbons occurring in the earth. In its narrower, commercial sense, petroleum is usually restricted to the liquid deposits known as crude oil, the gaseous ones being known as natural gas and the solid ones as bitumen or asphalt.

Most crude oils, although liquid as such, contain gaseous and solid hydrocarbons in solution. The gases come out of solution, either on the release of pressure as the crude oil is produced or during the first stages of refining, and contribute to the total natural gas production. Some of the solids are recovered during refining as bitumen and wax, some stay in solution in the liquid oil products. Natural gas may be found associated with crude oil as a gas-cap above the oil or on its own, unassociated with oil.

2.6.1 Origin and Occurrence of Petroleum

Origin

The origin of petroleum is one of the most complex problems of the modern science. There have been several attempts at formulating theories that describe the details of the origin of petroleum. They are broadly classified into inorganic and organic theories.

Inorganic theory

In 1886, for example, Berthelot considered acetylene the basic raw material and that crude oil constituent were produced from the acetylene.

Initially, inorganic carbides were formed by the action of alkali metals on carbonates after which acetylene was produced by the carbides with H_2O.

$CaCO_3$ + Alkali metal $\longrightarrow$ CaC_2 (calcium carbide).

$CaC_2 + H_2O \longrightarrow HC \equiv CH$ (acetylene) $\longrightarrow$ Petroleum

Another theory in which acetylene is also considered the basic material was described by Mendeleev, who proposed that the action of dilute acids or hot water on mixed iron and manganese carbide in the earth's bowel produces a mixture of hydrocarbon from which petroleum evolved:

$Fe_3C + H_2O + H^+ \longrightarrow$ hydrocarbon $\longrightarrow$ petroleum

$Mn_3C + H_2O + H^+ \longrightarrow$ HCS $\longrightarrow$ petroleum

Although such reactions do occur in principle, the carbide theory cannot explain the appearance in petroleum of an enormous number of HCS of diverse structure; it's also not clear how water could find its way from the region of low pressures in the earth's surface to the region of high pressures in it's bowels. Recent years have seen the advancement of other hypotheses postulating the cosmic, magnetic or volcanic origin of petroleum, but till date they have not gained popularity.

Organic theory

In 1911, Engler involved the concept of three separate stages of formation of petroleum.

In the first stage, animal and vegetable deposit accumulate in the bottom of inland seas (lagoon conditions) and are then decomposed by bacteria; the carbohydrates and the bulk of the protein are converted to water-soluble material or gases and thus removed from the sites. The fats, waxes, and other fat-soluble and stable materials (rosins, cholesterols) and others remain.

In the 2nd stage, high temperatures and pressures cause carbon dioxide to evolve from compounds from the hydroxyl-acids and alcohol to leave a bituminous residue. Continued application of the heat and pressures causes light cracking, producing a liquid product with high olefin content (protopetroleum).

In the third and last stage, the unsaturated components of the proto-petroleum are Polynesia wide the influence of contact catalysts and thus the polymerised are converted into paraffins and/or cycloparaffins (naphthenes). Aromatics were presumed to be formed either directly during cracking, by cyclisation through condensation reactions, or even during the decomposition of protein. The essential elements of this theory have survived. However, the main objection to a theory of this type is that the high-temperature sequence and the composition of the end product obtained in the laboratory experimental procedure carried out by Engler differ from that of petroleum, but tremendous progress has been made. However, whether crude is light or heavy, they both share a common theory of origin.

Some Basic Facts to Support the Organic Origin of Petroleum

1. The homologous series of hydrocarbons found in petroleum are found elsewhere only in organic matters and in obvious organic derivatives such as coal and carbonaceous shale.
2. Nitrogenous compounds, especially plant-derived porphyrins, comprise a small but significant portion of petroleums, elsewhere, porphyrins are found only as derivatives of chlorophylls and haemoglobins.
3. Easy cracking at temperature as low as $100^{o}C$.
4. Most petroleum deposits are associated with sedimentary rocks
5. The range of carbon isotope ratios (C^{13}/C^{12}) in petroleums is within the ranges of natural carbonaceous materials and is unlike such ratios in most inorganic matters. Most petroleum occurrences in igneous or metamorphic rocks may easily be explained migration from sedimentary rocks.
6. Many microscopic plants (diatoms) contain hydrocarbons.

7. Petroleum formation is proved to be normal and continuous process that has been in operation since the beginning of life and not process that requires severe sets of physicochemical conditions.

It is necessary to point out that numbers 2 and 3 are very relevant to the outcome of this research work. It is so, because contrary to the beliefs that crude oil fractional distillation is almost entirely physical phenomenon, in real practice it can be highly associated with some elements of cracking and indeed, the heavier the crude the higher the chance. This chance is essentially connected with asphaltenic, resinous and other organometallic compounds that are thermally unstable during distillation process. In essence cracking or ligand rupture (see pages 117) can bring about free radicals formation and their regrouping can lead to enhancement of light-ends recovery.

Occurrence of petroleum

Petroleum occurs in the earth's crust, in all possible states and varies in colour from light brown to dark brown or black, exhibiting luminescence in some cases. Normally heavy crudes tend to be darker than their corresponding light ones. This is because of the presence of high level of asphalthenic compounds in them (Figures 2.3 and 2.4).

Within the scope of this, work only heavy crudes within the API gravity range of 18 to 26 are considered.

2.6.2 Chemical Composition of Crude Oil

On a molecular basis, petroleum is a complex mixture of hydrocarbons with small amounts of organic compounds containing sulfur, oxygen, and nitrogen, as well as compounds

containing metallic constituents, particularly vanadium, nickel, iron, and copper. The hydrocarbon content may be as high as 97% w/w, for example in the lighter paraffinic crude oil or as low as 50% w/w in heavy crude oil and bitumen.

Nevertheless, crude oil with as little as 50% hydrocarbon components is still classified as a mixture of naturally occurring hydrocarbons. It will retain most of the essential characteristics of the hydrocarbons even though the non-hydrocarbon portion of the crude may actually consist of molecules containing one or perhaps two atoms of elements other than carbon and hydrogen (Gruse and Stevens, I960).

With the necessity of processing heavy oil, bitumen, and residue to obtain more gasoline and other liquid fuels, there has been the recognition that knowledge of the constituents of these higher boiling feedstocks is also of some importance. Indeed, the problems encountered in processing the heavier feedstocks can be equated to the chemical character and the amount of complex, higher-boiling constituents in the feedstock. Refining these materials is not just a matter of applying know-how derived from refining conventional crude oils but requires knowledge of the chemical structure and chemical behavior of these more complex constituents.

However, heavy crude oil and bitumen are extremely complex and very little direct information can be obtained by distillation. It is not possible to isolate and identify the constituents of the heavier feedstocks (using analytical techniques that rely upon volatility). Other methods of identifying the chemical constituents must be employed. Such techniques include a myriad of fractionation procedures as well as methods designed to draw inferences about the hydrocarbon skeletal structures and the nature of the heteroatomic functions.

Nevertheless, the theory that the petroleum precursors form a mix that is often referred to as protopetroleum (also referred to as primordial precursor soup or petroleum porridge*)* is an

acceptable generalization. And, the molecular types in any specified fraction is limited by the nature of the precursors of petroleum, their chemical structures, and the physical conditions that are prevalent during the maturation (conversion of the precursors) processes.

This concept has resulted in the consideration of petroleum as a continuum of molecular types and the nature of continuum is dictated by the proportions of the precursors that form the protopetroleum after which the prevalent conditions become operational in the formation of the final crude oil product. With this is mind, it might be anticipated that similar molecular types occur in heavy oil and bitumen as occurred in conventional petroleum. It then becomes a question of degree as well as molecular weight.

2.6.2.1 Ultimate (elemental) Composition

Despite the wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavier asphaltic crude oils at the other extreme (Erikh *et al*, 1988), it appears that of the data that are available, the proportions of the elements in petroleum vary over fairly narrow limits:

Carbon, 83.0-87.0%

Hydrogen, 10.0-14.0%

Nitrogen, 0.1-2.0%

Oxygen, 0.05-1.5%

Sulfur, 0.05-6.0%

Metals (Ni and V), <1000 ppm

Indeed, when the many localized or regional variations in maturation conditions are assessed it is perhaps surprising that the ultimate compositions are so similar. Perhaps this observation, more

than any other observation, is indicative of the similarity in nature of the precursors from one site to another.

Because of the narrow range of carbon and hydrogen content, it is not possible to classify petroleum on the basis of carbon content as coal is classified; carbon contents of coal can vary from as low as 75% w/w in lignite to 95% w/w in anthracite (Speight, 1994a). Of course, other subdivisions are possible within the various carbon ranges of the coals, but petroleum is restricted to a much narrower range of elemental composition.

2.6.2.2 Chemical Composition

The precise chemical composition of many of the heavier feedstocks is, despite the large volume of work performed in this area, largely speculative. As already noted, the composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells are more than likely to produce petroleum with very different characteristics.

In very general terms (and as observed from elemental analyses), petroleum, heavy oil, bitumen, and residua are a melange of: (1) hydrocarbons; (2) nitrogen compounds; (3) oxygen compounds; (4) sulfur compounds; and (5) metallic constituents. However, this general definition is not adequate to describe the composition of petroleum as it relates to the behavior of these feedstocks. Indeed the consideration of hydrogen-to-carbon atomic ratio, sulfur content, and API gravity are no longer adequate to the task of determining refining behavior.

Feedstock behavior during refining is better addressed through consideration of the molecular make-up of the feedstock (perhaps, by analogy, just as genetic make-up dictates human behavior). The occurrence of amphoteric species (i.e., compounds having a mixed acid/base nature) is not addressed nor is the phenomenon of molecular size or the occurrence of

specific functional types which can play a major role in the interactions between the constituents of a feedstock. All of these items are important in determining feedstock behavior during refining operations.

The hydrocarbon content of petroleum may be as high as 97% w/w (for example in the lighter paraffinic crude oils). It is, nevertheless, the nonhydrocarbon (sulfur, oxygen, nitrogen, and metal) constituents that play a large part in determining the processability of the crude oil (Gurevich, 1972; Rail *et al*., 1972). The inclusion of organic compounds of sulfur, nitrogen, and oxygen serves only to present crude oils as even more complex mixtures, and the appearance of appreciable amounts of these nonhydrocarbon compounds causes some concern in the refining of crude oils. Even though the concentration of nonhydrocarbon constituents (i.e., those organic compounds containing one or more sulfur, oxygen, or nitrogen atoms) in certain fractions may be quite small, they tend to concentrate in the higher boiling fractions of petroleum. Indeed, their influence on the processability of the petroleum is important irrespective of their molecular size and the fraction in which they occur.

2.6.2.3 Hydrocarbon Components

The study of the individual hydrocarbon constituents in petroleum began in the 1850s when alkylbenzenes were reported in a petroleum from Burma. Later, methylcyclopentane was isolated from a Caucasian petroleum, followed by the isolation of paraffin hydrocarbons from various petroleum fractions. Distillation techniques and the separation of cyclohexane by crystallisation of a distillate fraction into which it had been concentrated is an example of what could be accomplished at that early date. Nevertheless, the isolation of pure compounds from petroleum is an exceedingly difficult task, and the overwhelming complexity of the hydrocarbon constituents of the higher molecular weight fractions as well as the presence of compounds of

sulfur, oxygen, and nitrogen, are the main causes for the difficulties encountered. It is difficult on the basis of the data obtained from synthesized hydrocarbons to determine the identity or even the similarity of the synthetic hydrocarbons to those that constitute many of the higher boiling fractions of petroleum. Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups. Olefinic groups are not usually found in crude oils, and acetylenic hydrocarbons are very rare indeed. It is therefore convenient to divide the hydrocarbon components of petroleum into the following three classes:

1. *Paraffins,* which are saturated hydrocarbons with straight or branched chains, but without any ring structure.
2. Naphthenes*,* which are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as alicyclic hydrocarbons*)*.
3. Aromatics*,* which are hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinic side chains.

Paraffin Hydrocarbons: The proportion of paraffins in crude oils varies with the type of crude, but within any one crude oil, the proportion of paraffinic hydrocarbons usually decreases with increasing molecular weight (Figure 2.15). In the gasoline range, for instance, paraffin contents as high as 80% have been noted, whereas in the lubricating oil range a 30% w/w paraffin content is exceptionally high. In fact, many oils yield lubricating fractions that are totally devoid of paraffins.

The relationship between the various hydrocarbon constituents of crude oils is one of hydrogen addition or hydrogen loss (Figure 2.16), and there is no reason to deny the occurrence of these inter-conversion schemes during the formation, maturation, and in situ alteration of petroleum. Indeed, a scheme of this type lends even more credence to the complexity of petroleum within the hydrocarbon series alone.

Normal paraffin hydrocarbons (n-paraffins, straight-chain paraffins) occur in varying pro-

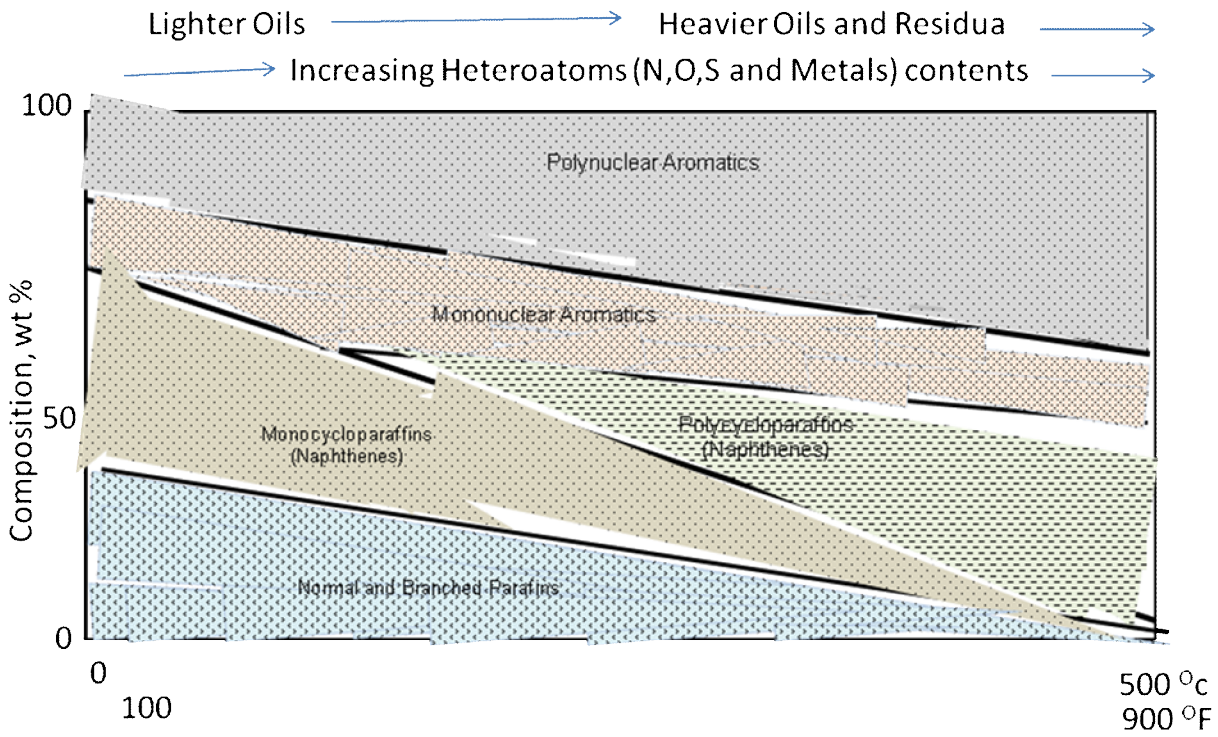


Figure 2.15: The Distribution of Various Compound Types throughout the Boiling Range of Petroleum

portions in most crude oils. In fact, paraffinic petroleum may contain up to 20-50% w/w *n*-paraffins in the gas oil fraction. One particular gas oil (boiling range 150-350°C, 300-660°F), contained every normal paraffin possible that could be present in this fraction. Furthermore, all the normal paraffins up to and beyond n-dodecane (12 carbon atoms) have been isolated from crude oil. However, naphthenic or asphaltic crude oils sometimes contain only very small

amounts of normal paraffins, as illustrated by the isolation of less than 1% of paraffins from Borneo crude oil.

Considerable quantities of iso-paraffins have been noted to be present in the straight-run gasoline fraction of petroleum. The 2- and 3-rnethyl derivatives are the most abundant, and the 4-methyl derivative is present in small amounts. If at all, and it is generally accepted that the slightly branched paraffins predominate over the highly branched materials. It seems that the n-paraffins occur throughout the boiling range of petroleum fractions. The proportion tends to decrease with increasing boiling point; it appears that if the iso-paraffms are present in lubricating oils their amount is too small to have any significant influence on the physical properties of the lubricating oils.

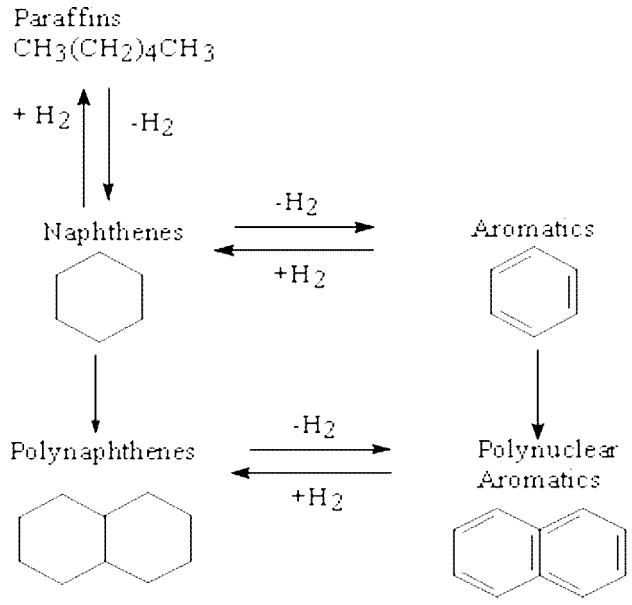


Figure 2.16: Interrelationship of the Various Hydrocarbon Compounds

Cycloparaffin Hydrocarbons (Naphthenes): Although only a small number of representatives have been isolated so far, cyclohexane-, cyclo-pentane-, and decahydronaphthalene derivatives are largely represented in oil fractions. Petroleum also contains polycyclic naphthenes, such as terpenes, and such molecules (often designated bridge-ring hydrocarbons) occur even in the

heavy gasoline fractions (boiling point 150-200°C, 300-390°F). Naphthene rings may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons there are individuals with rings of the three-, four-, five-, six-, seven-, and eight-membered type. It is now generally believed that oil fractions contain chiefly five- and six-membered rings. Only naphthenes with five- and six-membered rings have been isolated from the lower boiling fractions. Thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable. The naphthenic acids contain chiefly cyclic pentane as well as cyclohexane rings.

As the molecular weight (or boiling point) of the petroleum fraction increases, there is as well an increase in the amount of cycloparaffinic (naphthenic) species in the fraction.

In the asphaltene fraction, free condensed naphthenic ring systems may occur but general observations favor the occurrence of combined aromatic-naphthenic systems that are variously substituted by alkyl systems. There is also general evidence, that the aromatic systems are responsible for the polarity of the asphaltene constituents. The heteroatoms are favored to occur on or within the aromatic (pseudo-aromatic) systems.

Aromatic Hydrocarbons: Aromatic compounds are common to all petroleum and it is the difference in extension that becomes evident upon examination of a series of petroleum. By far the majority of these aromatics contain paraffmic chains, naphthene rings, and aromatic rings side by side.

There is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. However, aromatic hydrocarbons without the accompanying naphthene rings

or alkyl-substituted derivatives seem to be present in appreciable amounts only in the lower petroleum fractions.

In summation, all hydrocarbon compounds that have aromatic rings, in addition to the presence of alkyl chains and naphthenic rings within the same molecule are classified as aromatic compounds. Many separation procedures that have been applied to petroleum result in the isolation of a compound as an *aromatic* even if there is only one such ring (i.e., six carbon atoms) that is substituted by many more than six nonaromatic carbon atoms.

It should also be emphasized that in the higher boiling point petroleum fractions, many polycyclic structures occur in naphthenoaromatic systems. The naphthenoaromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher boiling point petroleum fractions.

From an examination of various functional subfractions, it was shown that amphoteric species and basic nitrogen species contain polycyclic aromatic systems having two-to-six rings per system. On the other hand, acid subfractions (phenolic/carboxylic functions) and neutral polar subfractions (amides/amino functions) contain few if any polycyclic aromatic systems having more than three rings per system.

Unsaturated Hydrocarbons: The presence of olefins (R – CH=CH-R') in petroleum has been under dispute for many years because there are investigators who claim that olefins are actually present; in fact these claims usually refer to distilled fractions, and it is very difficult to entirely avoid cracking during the distillation process. Nevertheless, evidence for the presence of considerable proportions of olefins in Pennsylvania crude oils!! has been obtained; spectroscopic and chemical methods showed that the crude oils, as well as all distillate fractions, contained up

to 3% w/w olefins. Hence, although the opinion that petroleum does not contain olefins requires some revision, it *is* perhaps reasonable to assume that the Pennsylvania crude oils may hold an exceptional position and that olefins are present in crudes in only a few special cases. The presence of dienes (R - CH=CH—CH=R') and acetylenes (RC≡C-R') is considered to be extremely unlikely. In summary, a variety of hydrocarbon compounds occur throughout petroleum. Although the amount of any particular hydrocarbon varies from one crude oil to another, the family from which that hydrocarbon arises is well represented.

2.6.2.4 Nonhydrocarbon Components

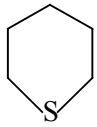
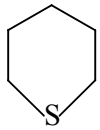
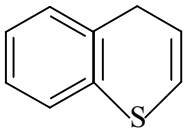
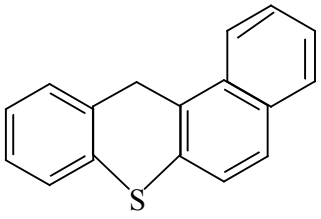
The previous sections present some indication of the types and nomenclature of the organic hydrocarbons that occur in various crude oils. Thus it is not surprising that petroleum which contains only hydrocarbons is, in fact, an extremely complex mixture. The phenomenal increase in the number of possible isomers for the higher hydrocarbons makes it very difficult, if not impossible in most cases, to isolate individual members of any one series having more than, say, 12 carbon atoms.

Inclusion of organic compounds of nitrogen, oxygen, and sulfur serves only to present crude oil as an even more complex mixture than was originally conceived. Nevertheless, considerable progress has been made in the isolation and/or identification of the lower molecular weight hydrocarbons, as well as accurate estimations of the overall proportions of the hydrocarbon types present in various petroleums. Indeed, it has been established that, as the boiling point of the petroleum fraction increases, not only the number of the constituents but the molecular complexity of the constituents also increases (Figure 2-15).

Crude oils contain organic nonhydrocarbon constituents, mainly sulfur-, nitrogen-, and oxygen-containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the nonvolatile residues.

In summary, nomenclature of some various types of organic sulphur, oxygen and nitrogen are hereby presented in Tables 2.7, 2.8 and 2.9 respectively.

Table 2.7: Nomenclature and Types of Organic Sulphur Compounds in Petroleum

RSH	Thiols (Mercaptans)
RSR`	Sulfides
	Cyclic Sulfides
RSSR`	Disulfides
	Thiophene
	Benzothiophene
	Dibenzothiophene

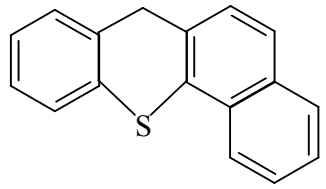
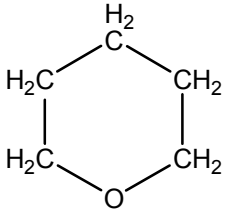
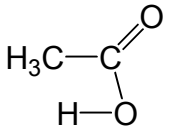
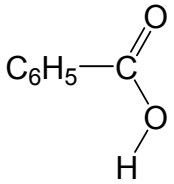
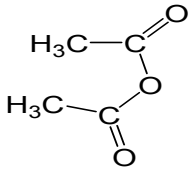
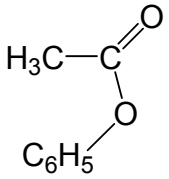
	Naphthabenzothiophene

Table 2.8: Nomenclature and Types of Organic Oxygen Compounds in Petroleum

Alcohols	
$CH_3 – O – H$	Methyl alcohol
$C_6H_6 – O – H$	Phenyl alcohol (phenol)
Ether	
$CH_3 – O – CH_3$	Dimethyl ether
$C_6H_5 – O – C_6H_5$	Diphenyl ether
Cyclic ether	
	Tetrahydropyran (pentamethylene oxide)
Carboxylic acids	
	Acetic acid
	Benzoic acid
Carboxylic acid Anhydrides	
	Acetic anhydride
Carboxylic acid Esters	
	Ethyl acetate

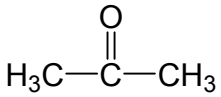
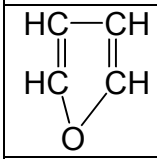
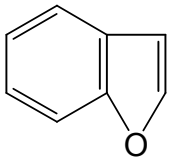
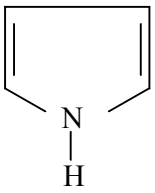
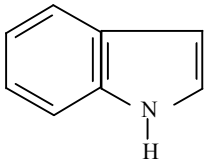
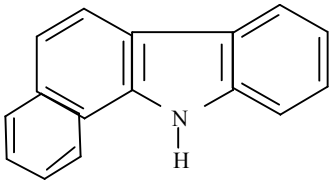
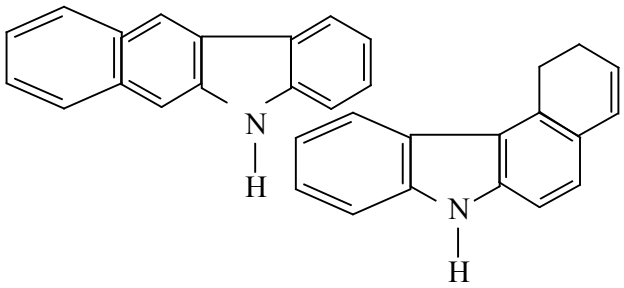
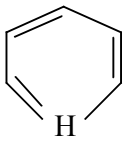
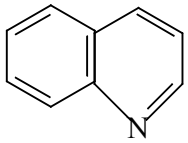
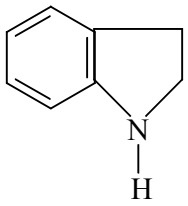
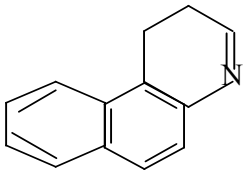
Ketones	
	Dimethyl ketone
Furans	
	Furan
	Benzofuran

Table 2.9: Nomenclature and Types of Organic Nitrogen Compounds in Petroleum

Nonbasic		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	

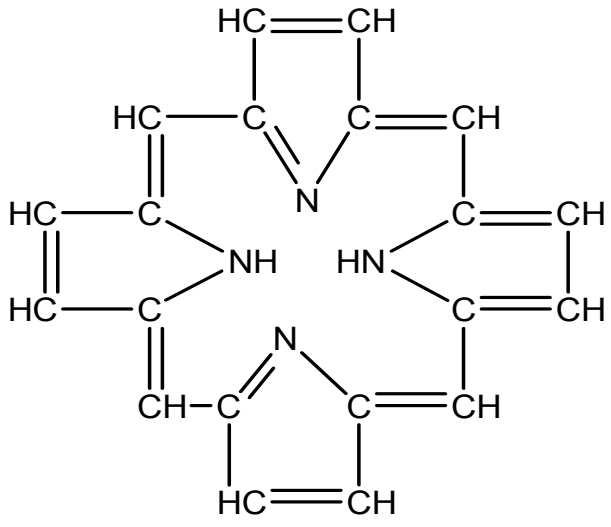
Benzocarbazole	$C_{16}H_{11}N$	
Basic		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Benzocarbazole	$C_{13}H_9N$	

2.6.2.5 Porphyrins

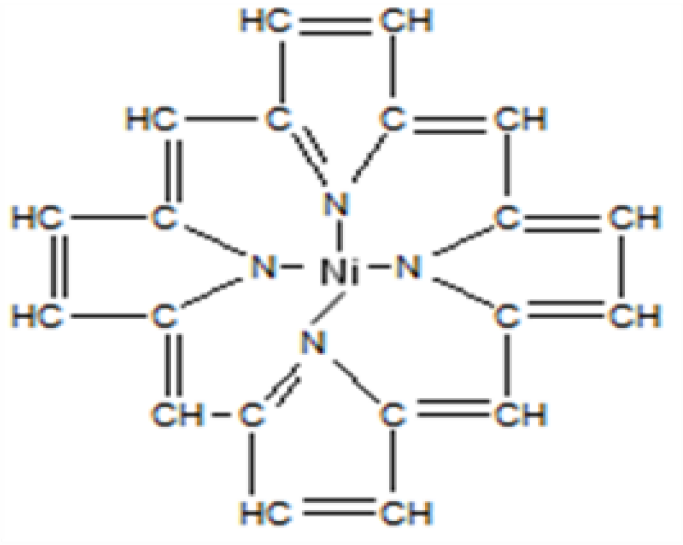
Treibs (1934), Glebovskaya and Volkenshtein (1948) all reported that porphyrins are a naturally occurring chemical species that have been known to exist in petroleum for more than

103years. They are given separate consideration in this section because of their uniqueness as separate and distinct chemical entities. They are not usually considered among the usual nitrogen-containing constituents of petroleum, but within the context of this work are considered a metallo-containing organic material that occurs in some crude oils. As a result of these early investigations there arose the concept of porphyrins as biomarkers that could establish a link between compounds found in the geosphere and their corresponding biological precursors.

Porphyrins usually occur in the nonbasic portion of the nitrogen-containing concentrate. The simplest porphyrin is porphine and consists of four pyrrole molecules joined by methine (—CH=) bridges (Figure 2.17). The methine bridges establish conjugated linkages between the component pyrrole nuclei, forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives increased aromatic character to the porphine molecule (Erikh *et al*, 1988).



(a)



(b)

Figure 2.17: The Structure of (a) Porphine and (b) the Nickel Chelate of Porphine

Of all the metals in the periodic table, only vanadium and nickel have been proven definitely to exist as chelates in significant amounts in a large number of crude oils and tar sand bitumen. The existence of iron porphyrins in some crudes has been claimed (Franceskin *et al*, 1986). Geochemical reasons for the absence of substantial quantities of porphyrins chelated with metals other than nickel and vanadium in most crude oils and tar sand bitumen have been advanced (Hodgson et al., 1967; Baker and Palmer, 1978; Quirke, 1987).

If the vanadium and nickel contents of crude oils are measured and compared with porphyrin concentrations, it is usually found that not all the metal content can be accounted for as porphyrins (Dunning *et al*., 1960; Reynolds, 1997). In some crude oils, as little as 10% w/w of total metals appears to be chelated with porphyrins. Only rarely can all measured nickel and vanadium in a crude oil be accounted for as porphyrinic (Erdman and Harju, 1963). Currently some investigators believe that part of the vanadium and nickel in crude oils is chelated with ligands that are not porphyrins. These metal chelates are referred to as nonporphyrin metal

chelates or complexes. Many of the other various types of porphyrins are shown in Figures 2.18 and 2.19.

On the other hand, the issue of nonporphyrin metal in crude oils has been questioned (Goulon et al., 1984). There is the possibility that in such systems as the heavy crude oils, in

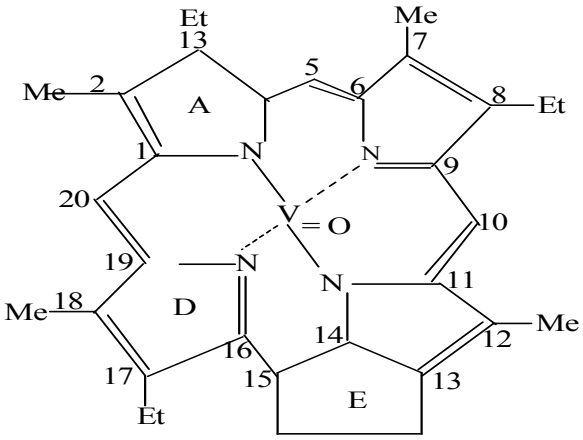


Figure 2.18: The Formalised Numbering of the Porphyrin System for Nomenclature

which intermolecular associations are important, measurement of the porphyrin concentrations are unreliable and there is a tendency to undercount the actual values. However, for the purposes of this chapter it is assumed that nonporphyrin chelates exist in fossil fuels but the relative amount is as yet unknown.

Finally, during the fractionation of petroleum the metallic constituents (metal-loporphyrins and nonporphyrin metal chelates) are concentrated in the asphaltene fraction. The deasphaltened oils (petrolenes and maltenes) contain smaller concentrations of porphyrins than the parent materials and usually very small concentrations of nonporphyrin metals.

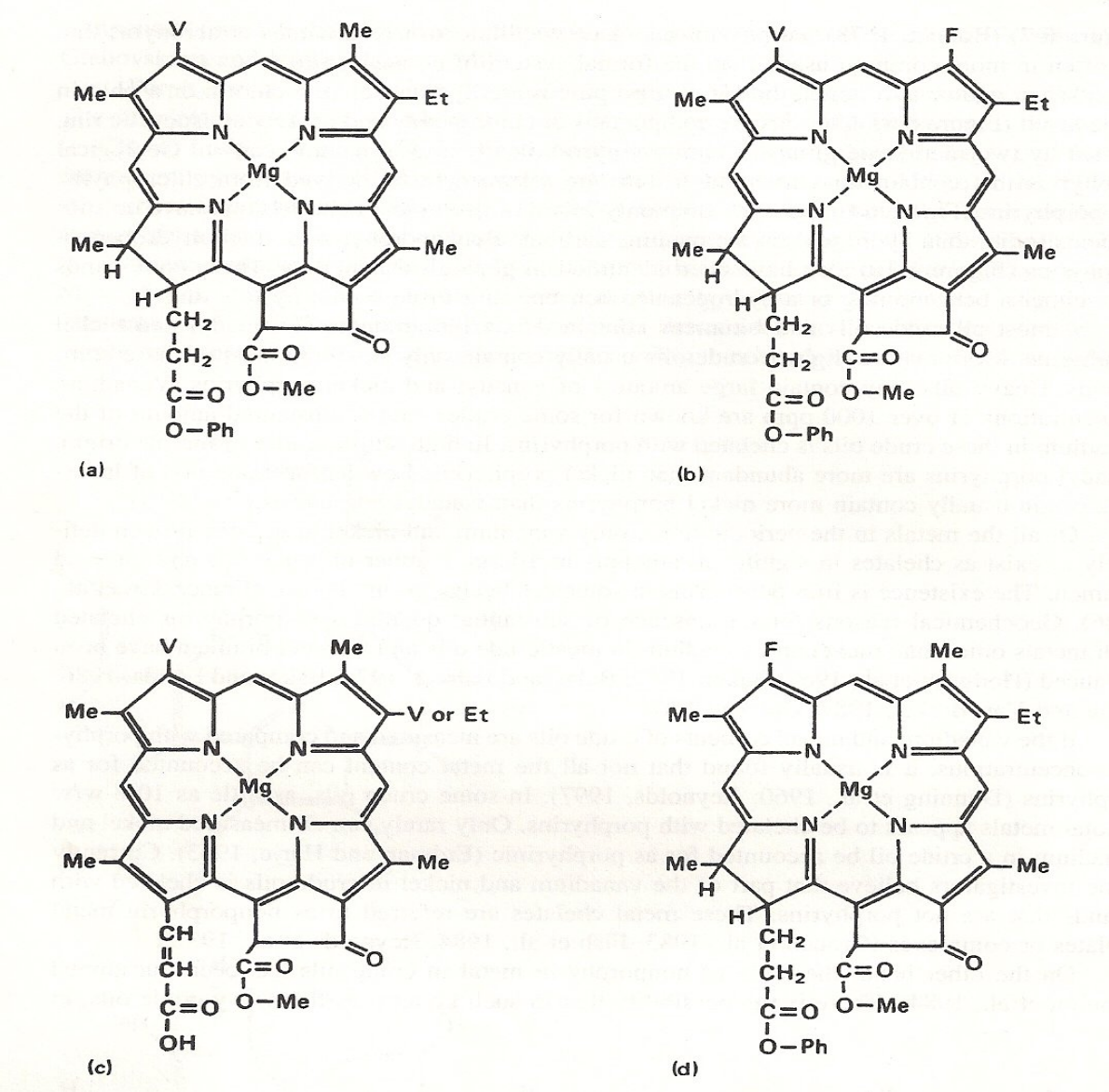


Figure 2.19: Representative Structures of Chlorins as Represented by Different Chlorophylls

Evidence for the presence of several other metals in oil-soluble form has been produced, and thus zinc, titanium, calcium, and magnesium compounds have been identified in addition to vanadium, nickel, iron, and copper. Examination of the analyses of a number of crudes for iron, nickel, vanadium, and copper indicates a relatively high vanadium content, which usually exceeds that of nickel, although the reverse can also occur.

Distillation concentrates the metallic constituents in the residues (Reynolds, 1997 and Yasuhiro *et al*, 2000), although some can appear in the higher boiling distillates, but the latter may be due in part to entrainment. Nevertheless, there is evidence that a portion of the metallic constituents may occur in the distillates by volatilization of the organometallic compounds present in the petroleum. In fact, as the percentage of overhead obtained by vacuum distillation of a reduced crude is increased, the amount of metallic constituents in the overhead oil is also increased. The majority of the vanadium, nickel, iron, and copper in residual stocks may be precipitated along with the asphaltenes by hydrocarbon solvents. Thus, removal of the asphaltenes with n-pentane reduces the vanadium content of the oil by up to 95% with substantial reductions in the amounts of iron and nickel.

It is very much probable that these compounds are thermally unstable and as such their cracking into simpler hydrocarbon molecules can contribute to/enhance the recovery of light-ends.

From what have been discussed generally in the literature survey of Section 2.6, two conclusions that have direct and positive bearings on the outcome on this work can be drawn:

1. Some of the hydrocarbon and non-hydrocarbon compounds that are found in petroleum can be polar or non-polar. Then, the question is how are they able to co-exist as one system without phase separation? The answer put forward by Unger and Andreeva (1995) is that the resultant force is in equilibrium with the forces of the individual component that constitute the system and that this resultant force is zero as expressed thus:

   $\sum_{i=1}^{n} Fi = 0$ ……..(2.0)

Therefore, if any external force whether physical, thermal, chemical, or introduction of substance, either originally present or foreign into the system, the equilibrium force would be weakened or at extreme situation broken down.

This work has explored a physical means of preliminarily weakening (Mohammed, 2001) the petroleum (heavy crude oil) system by the use of used engine oil thereby making easier the enhancement of the recovery of light-ends during atmospheric distillation process.

2. Towards the last part of Section 2.6. it was too, discussed and observed that many metallic and organometallic hydrocarbon compounds are vulnerable to thermal decomposition at elevated temperatures. The implication is that contrary to the general and popular beliefs that atmospheric distillation is almost entirely a physical phenomenon, this work hereby states that the resultant effects of thermal decomposition should not be underestimated. Indeed it has contributed to the enhancement of light-ends during distillation process as eventually proved in the atomic absorption spectrum (AAS) analysis of the residues that were derived from TBP distillation of the virgin crudes and their various blends. From Table 4.16, the metals that are reported from the AAS analysis of the residue must have been derived from thermal decomposition of the porphyrins and some other organometallic compounds (see page 117).

Finally before the literature review of the next section commences, it has to be stated that generally crude oil is indeed and will never be separated into component slate as discussed in the previous section. Instead, it is usually refined and further processed into many number of

products whose value is many times that of the original, especially for products like light-ends (gas, naphtha, kerosene and diesel) and the heavy ones (lubricating oil fractions and the asphalt).

As it is well known, crude oil refining process apart from preliminary treatments begins from atmospheric distillation and as reflected in the title of this research, distillation theoretical background and as a method of separation of light-ends from the heavier ones will be adequately covered in the next section of the work.

2.7 DESCRIPTION OF SEPARATION OF MIXTURES BY DISTILLATION

The general objective of distillation is the separation of substances that have different vapor pressures at any given temperature. The word *distillation* as used here refers to the physical separation of a mixture into two or more fractions that have different boiling points.

If a liquid mixture of two volatile materials is heated, the vapor that comes off will have a higher concentration of the lower boiling material than the liquid from which it was evolved. Conversely, if a warm vapor is cooled, the higher boiling material has a tendency to condense in a greater proportion than the lower boiling material. The early distillers of alcohol for beverages applied these fundamental ideas. Although distillation was known and practiced in antiquity and a commercial still had been developed by Coffey in 1832, the theory of distillation was not studied until the work of Sorel in1893. Later other outstanding workers in this field were Lord Rayleigh in 1902 and Lewis in 1909. Current technology has permitted the large-scale separation by distillation of ethylbenzene and p-xylene, which have only a 3.9°F difference in boiling points (Anderson *et al*, 1960).

Usually a distillation column consists of a series of plates (or trays) and in normal operation, there is a certain amount of liquid on each plate, and some arrangement is made for

ascending vapors to pass through the liquid and have intimate contact with it. The descending liquid flows down from the plate above through a downcomer, across the next plate, and then over a *weir* and into another downcomer to the next lower plate as shown in Figure 2.20. For many years, *bubble caps* were used (of which a variety of designs are shown in Figure 2.21) for contacting the vapor with the liquid. These contacting devices promote the production of small bubbles of vapor with relatively large surface areas.

Recent developments of devices for contacting the vapor and liquid streams have tended to displace bubble caps. New columns are usually equipped with either ballast trays (see Figure 2.22), sometimes called valve trays or perforated trays (see Figure 2.23), sometimes called *sieve trays*. *In* the valve trays, the valve opens wider as the vapor velocity increases and closes as the vapor velocity decreases. This opening and closing allows the valve to remain immersed in liquid and thereby preserve a liquid seal over wide ranges of liquid and vapor flow rates.

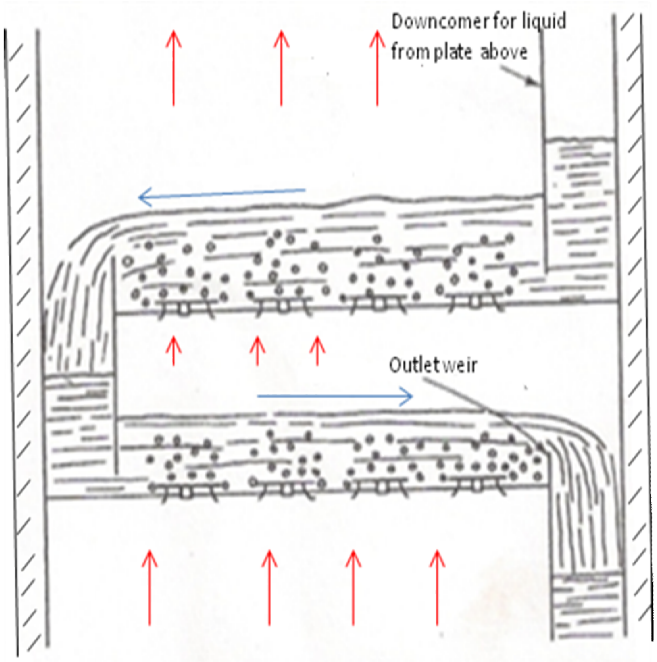


Figure 2.20: The Interior of a Distillation Column

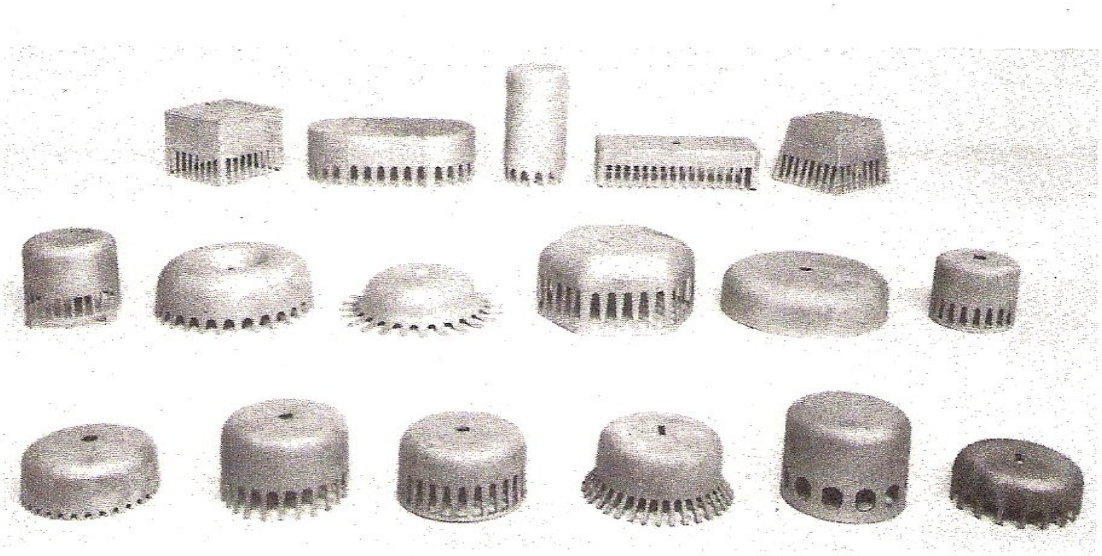


Figure 2.21: Various Types of Bubble Caps used in Distillation Column

As indicated in Figure 2.24, the overhead vapor V_1, upon leaving the top plate enters the condenser where it is either partially or totally condensed. The liquid formed is collected in an accumulator from which the liquid stream L_o (called reflux*)* and the top product stream *D* (called the distillate*)*, are withdrawn. When the overhead vapor V_1 is totally condensed to the liquid state and the distillate *D* is withdrawn as a liquid, the condenser is called a total condenser.

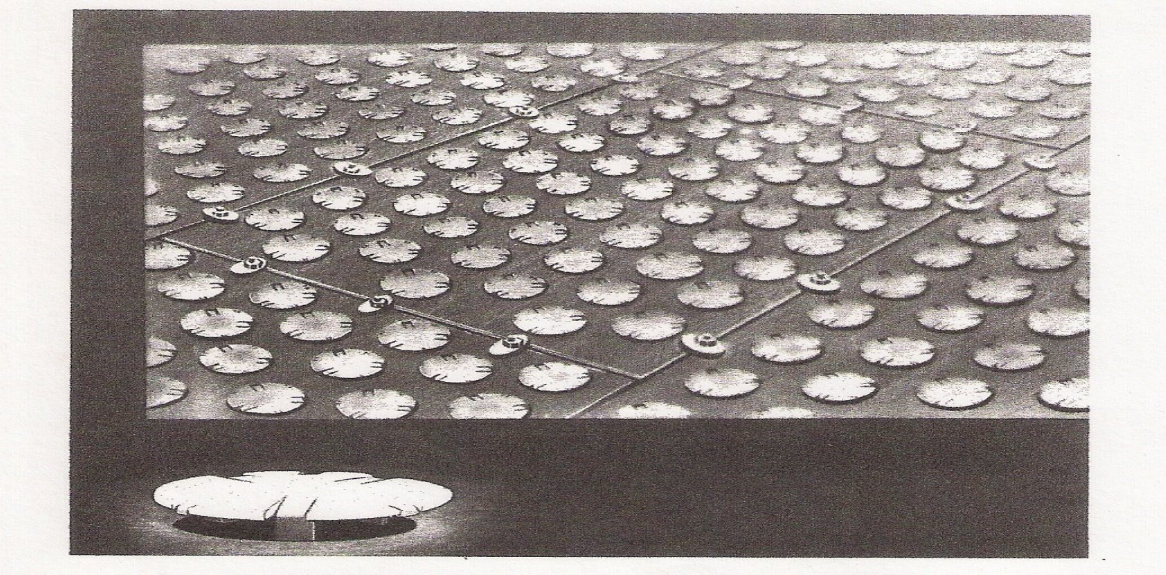


Figure 2.22: Portion of a Glitsch V-1 Ballast Tray

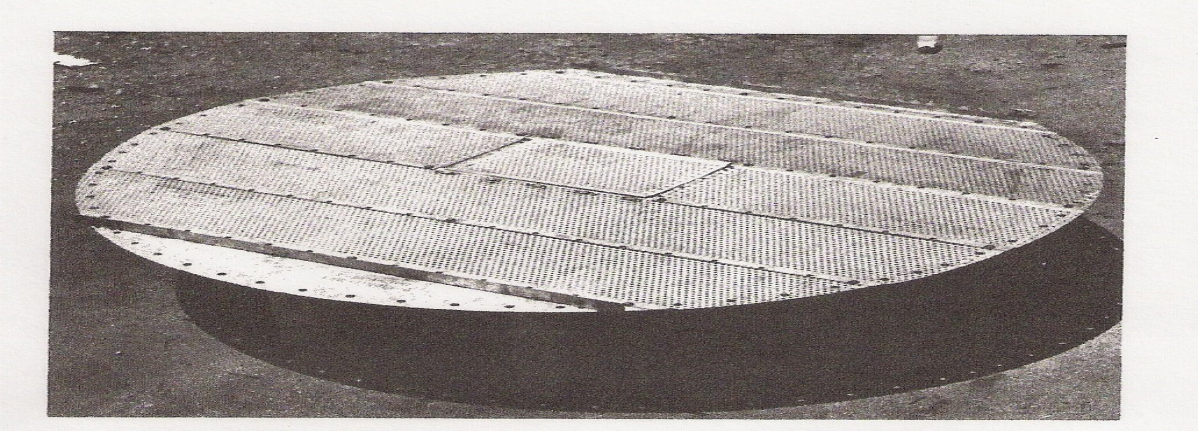


Figure 2.23: A Perforated or Sieve Tray

If V_1 is partially condensed to the liquid state to produce the reflux L_0 and the distillate D is withdrawn as a vapor, the condenser is called a *partial condenser.* The amount of liquid reflux is commonly expressed in terms of the *reflux ratio,* L_0/D. Although the internal liquid to vapor ratio, L_0/V, is sometimes referred to as the internal reflux ratio, the term *reflux ratio* will be reserved herein to mean L_0/D.

The liquid that leaves the bottom plate of the column enters the reboiler, where it is partially vaporized. The vapor produced is allowed to flow back up through the column, and the liquid is withdrawn from the reboiler and called the *bottoms* or *bottom product B.* In practice, the reboiler is generally located externally from the column.

2.7.1 Fundamental Principles Involved in Distillation

To compute the composition of the top product D and the bottom product B which may be expected by use of a given distillation column operated at a given set of conditions, it is necessary to obtain a solution to the following expressions:

1. Equilibrium relationships
2. Component-material balances
3. Total-material balances
4. Energy balances

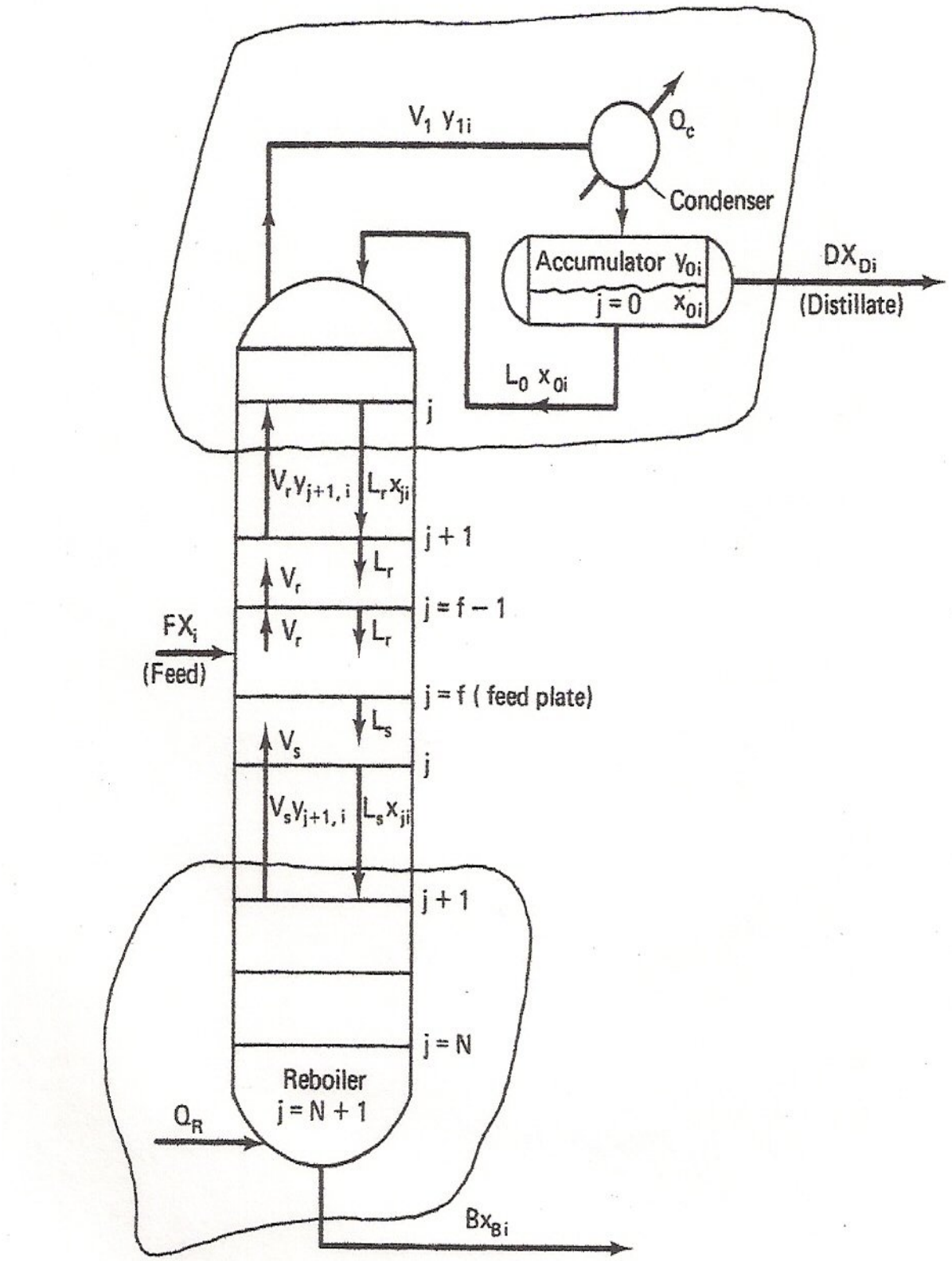


Figure 2.24: Sketch of a Conventional Column in which the Total Flow Rates are Constant within the Rectifying and Stripping Sections

2.7.1.1 Physical Equilibrium

A two-phase multicomponent mixture is said to be in equilibrium if the following necessary conditions are satisfied (Denbigh, 1955).

1. The temperature T^v of the vapor phase is equal to the temperature T^L of the liquid phase.

2. The total pressure P^v throughout the vapor phase is equal to the total pressure P^L throughout the liquid phase. …… (2.1)

3. The tendency of each component to escape from the liquid phase to the vapor phase is exactly equal to its tendency to escape from the vapor phase to the liquid phase.

In the following analysis it is supposed that a state of equilibrium exists,

$T^v = T^L = T$, $P^v = P^L = P$.

and the escaping tendencies are equal.

Now consider the special case in which, the third condition may be represented by Raoult's law:

$Py_i = P_i x_i$ ……..(2.2)

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, and P_i is the vapor pressure of pure component *i* at the temperature *T* of the system.

The separation of a binary mixture by distillation may be represented in two-dimensional space, but dimensional space is required to represent the separation of a multicomponent mixture. The classical graphical method proposed by McCabe and Thiele since 1925 for the solution of problems involving binary mixtures is presented in a subsequent section. The McCabe-Thiele method makes use of an equilibrium curve that may be obtained from the "boiling point diagram".

2.7.1.2 Construction and Interpretation of the Boiling Point Diagram for Binary Mixtures

When a state of equilibrium exists between a vapor and liquid phase composed of two components *A* and *B,* the system is described by the following set of independent equations,

$$Py_A = P_A x_A$$

Equilibrium relationships: $$Py_B = P_B x_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.3)$$

$$y_A + y_b = 1$$

$$X_A + X_b = 1$$

where it is understood that Raoult's law is obeyed. Since the vapor pressures P_A and P_B depend on *T* alone, Equation (2-3) consists of four equations in six unknowns. Thus, to obtain a solution to this set of equations two variables must be fixed. (Observe that this result is in agreement with the Gibbs phase rule: f + v = c + 2. For the above case, the number of phases (f = 2, the number of components *c* = 2, and thus the number of degrees of freedom v = 2, that is, the number of variables that must be fixed = 2.)

The solution of the expressions given by Equation (2-3) for X_A in terms of P_A, P_B, and *P* is effected as follows. Addition of the first two expressions followed by the elimination of the sum of the y's by use of the third expression yields

$$P = P_A X_A + P_B X_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.4)$$

Elimination of X_B by use of the fourth expression given by Equation (2-3) followed by rearrangement of the result so obtained yields:

$$X_A = \frac{P - P_B}{P_A - P_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.5)$$

From the definition of a mole fraction ($0 \leq X_A \leq 1$), Equation (2-5) has a meaningful solution at a given *P* for any *T* lying between the boiling point temperatures T_A and T_B of pure *A* and pure

B, respectively at T_A, $P_A = P$, and at T_B, $P_B = P$. After X_A has been computed by use of Equation (2-5) at the specified P and T, the corresponding value of y_A which is in equilibrium with the value of X_A so obtained is computed by use of the first expression of Equation (2-3), namely,

$$y_A = \left(\frac{P_A}{P}\right) X_A \quad \ldots \ldots (2.6)$$

By plotting *T* versus X_A and *T* versus y_A, the lower and upper curves, respectively, of Figure 2.25 are typical of those obtained when component *A* is more volatile than *B*.

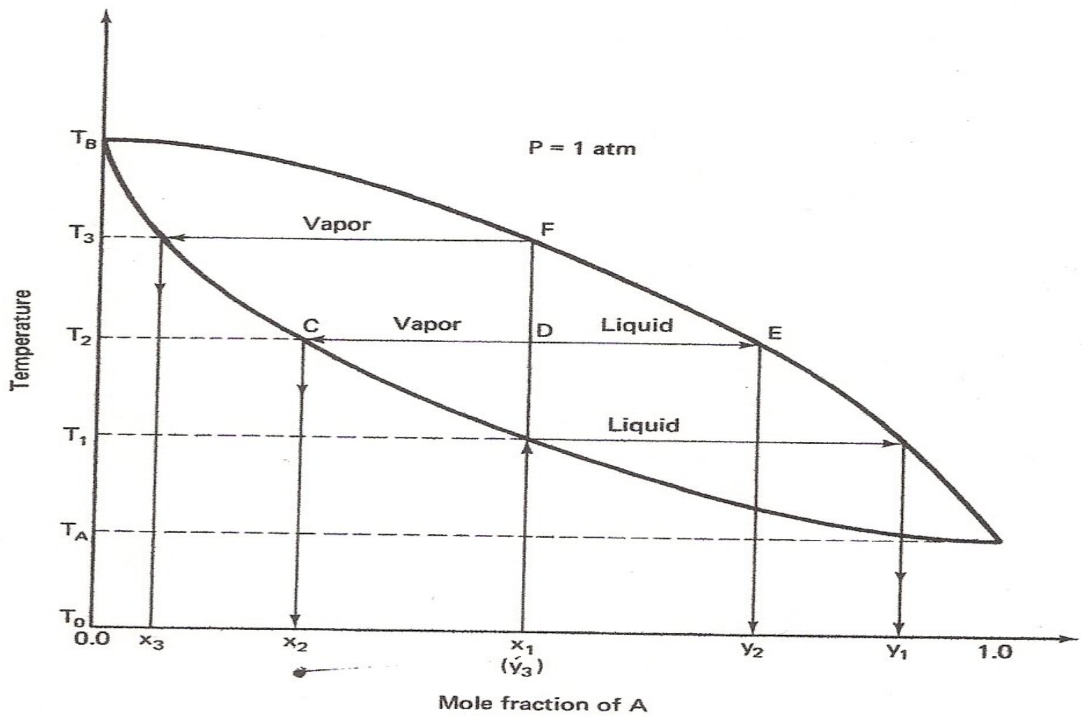


Figure 2.25: The Boiling Point Diagram

Component *A* is said to be more volatile than component *B,* if for all *T* in the closed interval $T_A \leq T \leq T_B$, the vapor pressure of *A* is greater than the vapor pressure of *B,* that is, $P_A > P_B$. The parallel lines such as *CE* that join equilibrium pairs (x, *y),* computed at a given *T* and *P* by use of Equations (2-5) and (2-6), are commonly called *Tie lines.* In essence a boiling point diagram is a most convenient aid in the visualization of phase behavior.

CHAPTER THREE

3.0 EXPERIMENTAL

This chapter gives the list and descriptions of the major sets of instruments /equipment, materials and the methodology that were employed in this work.

3.1 Instrument

The major components of the instruments that were very useful in this work are as discussed below. They are mostly pyrex glasswares that were assembled together in the fabrication of the true boiling point (TBP) distillation apparatus and other supporting items such as loading balance, thermometers, heating mantle, thermocouple, etc. Their main features are hereby described in Table 3.1

Table 3.1: List of Instruments and their Major Specifications

S/No.	Instrument	Description	Manufacturers
1	Mettler top-loading balance	Model Mettler P.1210, S/No. 5309779, Range: 0-1200g, Sensitivity: +/- 0.0005g	Mettler Instrumenter, B.U. Arnhem, Switzerland
2	Beakers	Pyrex, 1000/10, Range: 5-5000ml	CORNING Laboratory Division, England
3	Condensers	Pyrex, 1750/02, Graham (spiral form), 1730/04-liebig, 1740/04-allihn	----------II----------
4	Filter funnel	Pyrex, 2110/04-08	----------II----------
5	Sintered glassware	Pyrex, Porosity grade-0 and pore-size index (micron): 150-250	----------II----------
6	Buchner filter	Pyrex, 3700/04, Capacity: 200ml	----------II----------
7	Separating funnel (conical)	BS 2021, Pyrex, 2190/02, Capacity: 100ml	----------II----------
8	PTFE key stop cock	Pyrex, 2262/03, Length: 25mm	----------II----------
9	Measuring cylinder	BS 604, Pyrex, 3200/16, Range: 5-200ml	----------II----------
10	Reduction adapters	Quickfit, DA, Socket size range: 10/19-34/35	----------II----------

11	Expansion adapters	Quickfit, XA, Socket size range: 14/23-40/38	----------II----------
12	Multiple adapters	Quickfit, MA 4/23	----------II----------
13	Socket/cone adapters with 'T' connection	Quickfit, Range: MF 17/1- MF 17/3 and MF 18/2- MF 18/44	----------II----------
14	Bends with vent	Quickfit, Range: RA2/00-RA2/44	----------II----------
15	Plain bends, short	Quickfit, Range: RA1/01-RA/04	----------II----------
16	Liebig condenser	BSS 3787, Quickfit, Range: C1/00- C1/56	----------II----------
17	Coil condenser (reversible)	BSS 3787, Quickfit, Range:	----------II----------
18	Round bottom, Three necks-centre neck and two angled neck	Quickfit, FR 2L/3US/22A, capacity: 2000ml	----------II----------
19	Round bottom, Three necks-all parallel	Quickfit, FR 2L/5S/33P, Capacity: 200ml	----------II----------
20	Polythene reservoir bottles	BS 846, E-mil, PBM/500	----------II----------

3.1.1 Measuring and Heating Instrument

The major sets of measuring and heating instruments that were employed in the work are as briefly described in Table 3.2.

Table 3.2: List of Heating and Measuring Instrument

S/No.	Instrument	Description	Manufacturers
1	Thermometers	E-mil, P10699, Temperature range: 0-360^{o}C	----------II----------
2	Heating mantle	VDE SS 0721, Electrothermal, 90 10 06	Rudolf Brand, Wertheim, Germany
3	Thermocouple	MAS 838, Temprature range: 0-1000^{o}C (K-type)	MASTECH, Republic of China.

3.2 Equipment

The complete sets of equipment that were employed in the work are spectrophotometer, true boiling points (TBP) distillation apparatus and atomic absorption spectrometer (AAS)

machine. The plate, sketch, manufacturer and the basic principle on how they operate are hereby presented below.

a) Spectrophotometer (Henous γ, Germany)

With reference to Figures 2.56 and 3.1, the spectrophotometer quantitatively compares the fraction of light that passes through a reference solution (kerosene as a blank) and a test solution (crude oil sample or the blends with UEO) in the cuvette. Light from the source lamp is passed through a monochromator, which diffracts the light into a "rainbow" of wavelengths and outputs narrow bandwidths of this diffracted spectrum. Discrete frequencies are transmitted through the test sample. Then the intensity of the transmitted light is measured with a photodiode and the transmittance value for this wavelength is then compared with the transmission through a reference sample. In short, the sequence of events in a spectrophotometer is as follows:

1. The light source shines into a monochromator.
2. A particular output wavelength is selected and beamed at the sample.
3. The sample absorbs light.

In essence this spectrophotometer is a photometer (a device for measuring light intensity) that can measure (spectrophotometry-wikipedia,the free encyclopedia.mht., 2010) intensity as a function of the color (or more specifically the wavelength) of light. This important characteristic was adapted in measuring the absorbance of crude oil or blended samples with UEO. Hence, the absorbance was further mathematically manipulated to calculate the particle sizes as precursor for the choice of blend for TBP distillation (refer to page 125 and Appendix I).



Figure 3.1: Spectrophotometer Machine. Henous γ, Germany

b) True Boiling Point (TBP) Distillation Apparatus

TBP distillation apparatus is employed in the distillation of the crude oil and the various blends with used engine oil. It was fabricated in the department. It is compatible with ASTM D2864. The photo representation and the basic design features as well as principle of operation which have been adequately covered in Chapter Two are hereby shown in Figures 3.2 and 3.3 (refer to page 83).

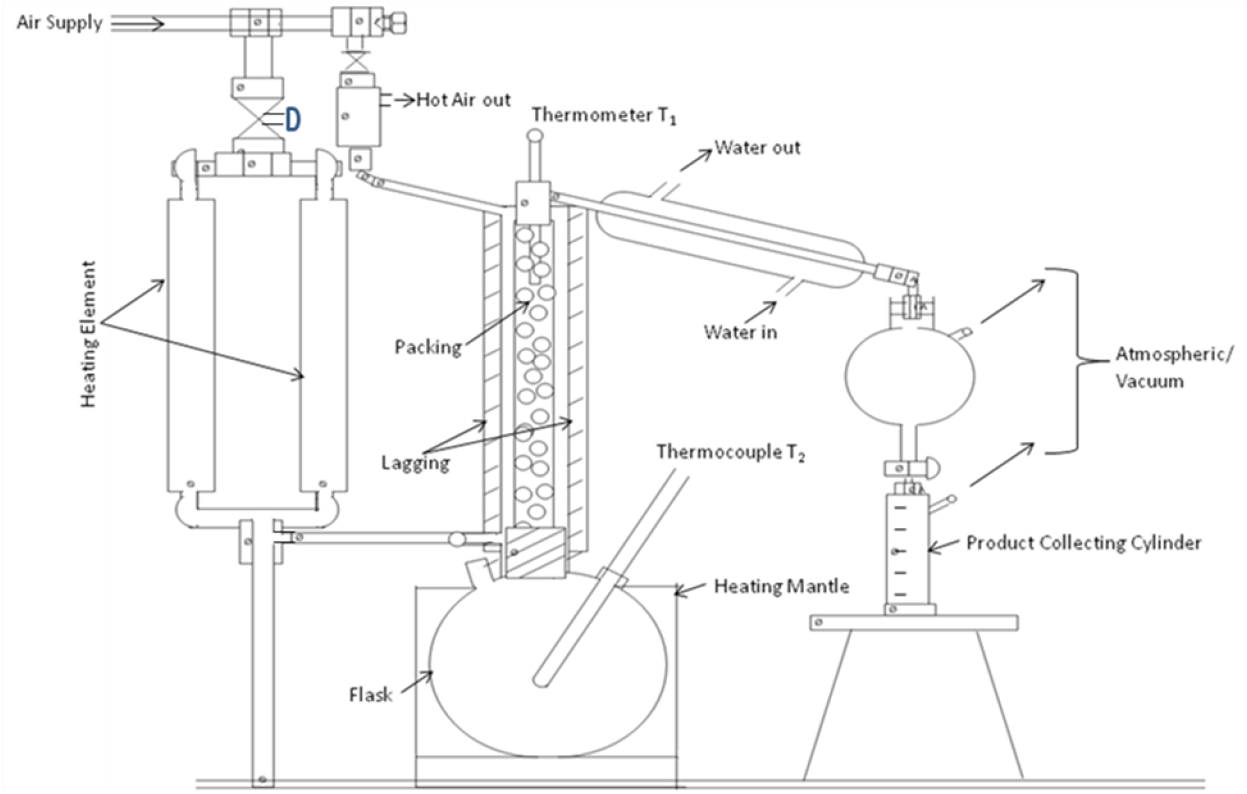


Figure 3.2: The Design Feature and Principle of Operation of the TBP Apparatus



Figure 3.3: True Boiling Point Distillation Apparatus as Assembled in the Department

c) **Atomic Absorption Spectroscopic (AAS) Machine**

The AAS was employed in analyzing and measuring in the sample (long residue of pure and blended crudes with UEO) the various amount of metals that were freed from the porphyrins. In principle the technique makes use of absorption spectrometry to assess the concentration of an analyte in the sample. In short, the electrons of the atoms in the atomizer could be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity. This analysis was carried out in Research and Development Unit of Nigerian National Petroleum Corporation (NNPC), Port

Harcourt, Rivers State, Nigeria. The photo sketch and principles of operation are shown in Figure 3.4 (refer to page 113).

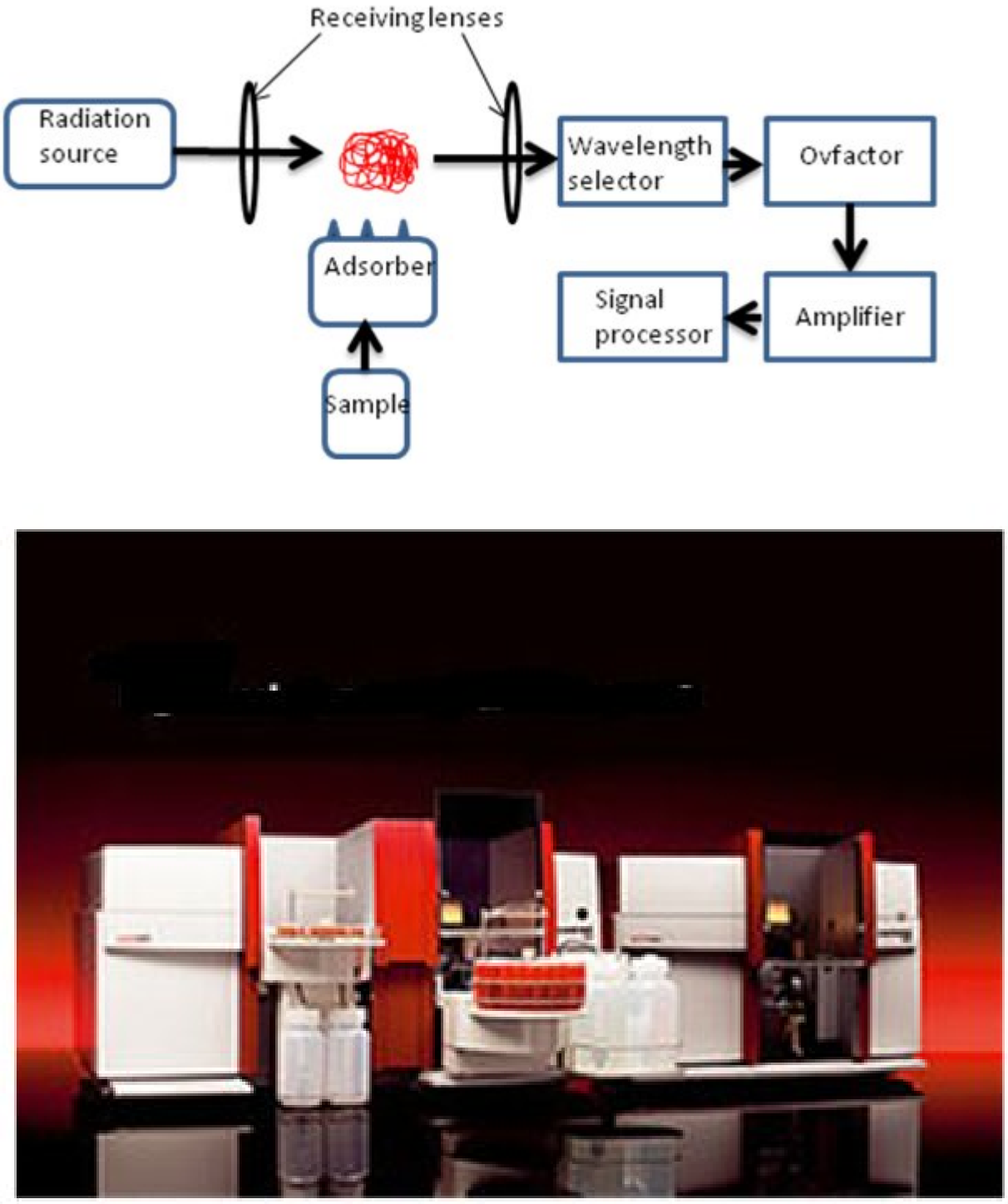


Figure 3.4: Design Features, Principle of Operation and Photo Sketch of the AAS

3.3 Materials

The main materials that were employed in this research work are mostly the raw feeds such as the heavy crude oil samples, used engine oil samples and kerosene, as well as chemical reagents like sodium metasilicate and ferric sulphate. Their major role in the work shall be adequately covered in Chapter Four. Here they are briefly mentioned and described as follows:

i) Heavy crude oil samples which include: Venezuela, Antan, and mixed (Venezuela and Antan in a ratio of 50/50% wt.)

ii) Used Engine Oil

iii) Kerosene was employed as blanks while carrying out the spectrophotometric analysis of the various blends.

iv) Sodium Metasilicate was used for absorption of residual water that was left after coagulation and sedimentation steps during the process of regeneration of UEO.

v) Ferric Sulphate was for coagulation and sedimentation of residual sludge during the process of regeneration of UEO.

3.4 METHODOLOGY

Below is the stage wise and sequential description of the procedures that were followed in this research work:

A. DATA COLLECTION

i. Used Engine Oil (UEO) Sample Collection

ii. UEO Pretreatment (Regeneration)

iii. Heavy Crude Oil Sample Collection

iv. Blending of Crude Oil Samples and UEO

B. DATA GENERATION

i. Determination of Average Particle Size (Diameter) of Crude Oil Samples and the Various Blends with UEO.

ii. True Boiling Point (TBP) Distillation of Pure and Blended Crude Samples.

C. DATA ANALYSIS

i. Atomic Absorption Spectroscopy (AAS) Analyses of the Long Residue (Fractional Cuts >360^{o}C).

3.4.1 Data Collection

UEO Sample Collection: This exercise involved the collection of UEO samples from Lube Bay automobile mechanic workshop of Oando Filling Station in Samaru, where the disposal of UEO by some motorists in Zaria is carried out. For specification purpose the samples of UEO collected were the ones of SAE 40 standards, have covered a mileage of maximum of ten thousand (10 000) kilometers and from light vehicles (Honda, Toyota, Mercedes, etc.) whose engine was manufactured from around 1992 (Momoh *et al*, 2005) up to now. This specification is necessitated by the fact that in case this research is scaled up, the availability of such UEO would not pose a problem.

UEO Pretreatment (Regeneration):

1. Settling: This is a method by which the UEO obtained in previous step is poured in a cone-shaped flask, without agitation for 48hrs to permit water and solid impurities to settle out and later decanted. The criterion for this separation is based upon the difference in specific gravity of water, solid impurities and oil. However, sludge and products of

oxidation which have about the same density like the oil are not readily removed until the next step is carried out.

2. Coagulation: To the recovered oil from settling method is added 2ml of ferric sulphate to every 20litres of the decanted oil. From here it's thoroughly mixed and allowed for another 24hrs for coagulation and agglomeration of any leftover heavy solid contaminants.
3. Sedimentation/Decantation: Here, the same step as in No. 1 is followed for the removal of sludge and products of oxidation.
4. Magnetisation: The recovered oil was then separated from the metal contaminants by dropping a magnet tied to a rope and then lowered inside a beaker containing the oil. The magnet is swirled for about 20 minutes inside the oil and then repeated for all the other samples. In this way almost or virtually all the metal contaminants are removed.
5. Thermal Treatment: Finally the UEO is heated to a temperature of 160^{o}C to drive off the light component hydrocarbon that was formed when used in the engine.

Crude Oil Sample Collection: The main source of crude oil samples that were used in this work is the Kaduna Refining and Petrochemical Company Ltd, Kaduna. The samples collected are Venezuela and Antan heavy crude oils.

The main property of crude oil required as data collection at this level is the specific gravity of the various samples of the crude. This is necessary to define the API gravity of various crude samples.

Blending of Crude Oil and UEO: Here, 30 sample bottles were prepared and labeled 1-30% wt/wt. UEO and crude oil blend. Each of the samples was mechanically mixed and allowed to stand for 24hrs for homogeneity. From this point the blends were ready for spectrophotometric analysis for the determination of particle diameter.

3.4.2 Data Generation

Determination of Average Particle Size (Diameter) of Blended Crude Oil Samples and UEO: The average particle sizes of blended crude oil samples were determined with Henous γ spectrphotometer. The working principle has been discussed in Chapters 2.0 and 3.0. Kerosene as a colourless solvent was used as blank in the cuvette. An average of 0.0403g of the blend was mixed with 6.3807g of kerosene. The absorbance at the wavelengths of 580nm and 620nm (Mohammed, 2001) of the individual sample was generated. This was mathematically processed to determine the average particle size of the various samples. The results are listed in Tables 4.1, 4.6 and 4.11 and Figures 4.1, 4.6 and 4.11. These results formed the basis on which the blend was selected for TBP distillation. To be precise, for Venezuela heavy crude, the blends which correspond with maximum and minimum particles diameter, i.e. 1% and 12% respectively were selected. Meanwhile, the pure crude, i.e. 0% blend acted as control. The same reason was extended to other crude and their blends. The fundamental principle and theory behind this approach was to establish the role the particle diameter of a blend in the enhancement and recovery of the lighter ends during distillation process.

True Boiling Point (TBP) Distillation of Pure and Blended Crude Samples: Each of the volume apparatus was ensured clean and dry. The round bottom flask containing a magnetic rod that

acted as stirrer was weighed empty and the required sampled charged in. The weight of the flask, rod and sample was then taken and the difference noted. The flask and its content was placed in the heating mantle. The arrangement in Figure 3.2 above was strictly followed.

The heating mantle was switched on and the sample distilled based on fractional cuts. Different receiving flasks were used to collect different boiling cuts and labeled accordingly. The weight of the receiving flask and the fractional cut was each time taken to obtain the weight of individual distillate.

When all the fractional cuts in IBP-350^{o}C were collected, the equipment was switched off, the still and the residual sample in it was allowed to cool and their collective weight measured. From this, the weight of the residue was calculated.

The same procedure was employed for each of the selected blended samples of the various crude oils.

At the end of each distillation session, a material balance was carried out to calculate the yield of each sample. These are shown in Tables 4.2, 4.3, 4.4, 4.7, 4.8, 4.9, 4.12, 4.13 and 4.14.

3.4.3 DATA ANALYSIS

The data analyzed was the determination of the metals that were 'freed' by the unavoidable thermal cracking of the pophyrin in the residue. As earlier mentioned this was carried out in Research and Development Unit, a subsidiary of Nigerian National Petroleum Corporation (NNPC) at Port Harcourt, Rivers State, Nigeria. The mode of operation was as earlier discussed in Chapter Two.

In summary all the steps described above can be represented in a flow chart as shown in Figure 3.5.

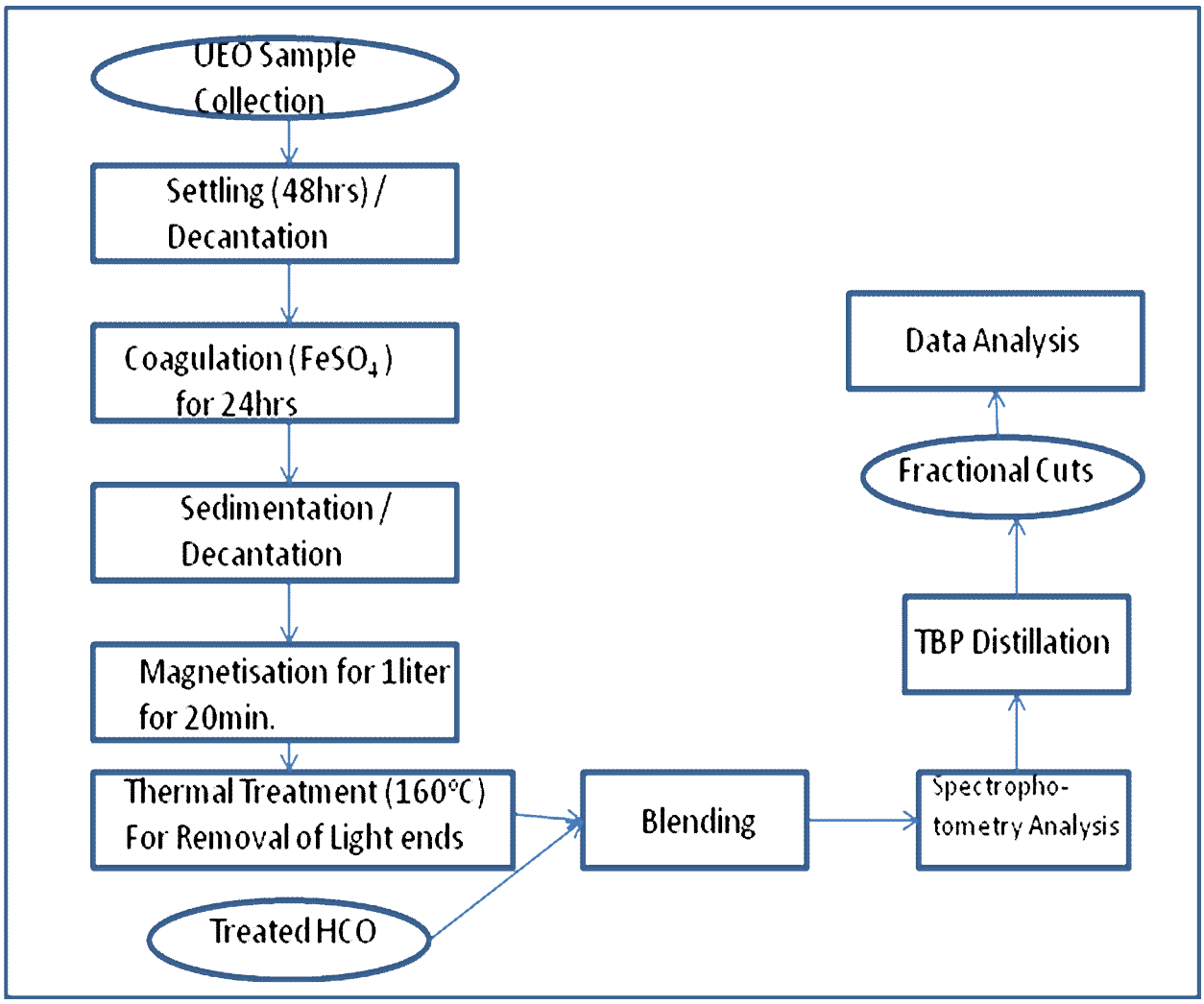


Figure 3.5: Process Flowchart

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

This chapter presents the results of various analyses that were carried out in the course of the research. Specifically the chapter begins from presentation of the tabular results of the average particle size of the various heavy crudes and their blends with the aid of spectrophotometric analyses, which acts as basis for selection of the blends for TBP distillation exercise.

The calculation of the average particle size is gotten from the relationship:

$$d = {}^{6000}/_{\rho * S} \quad \text{.....(5.1)}$$

Where, d is the average particle diameter of crude, ρ is the average density of the resin-asphalthenic compounds in the pure crude or the various blends and S is the average specific surface area of the crude or the various blends, which is given as,

$$S = 8.08\ x\ 10^3 B$$ (Mohammed, 2001)

And B as coefficient given as,

$B = (\log D_1 - \log D_2) / (\lambda_2 - \lambda_1)$,

Where, D_1 is the absorbance at wavelength, λ_1=620nm and D_2 is the absorbance at wavelength, λ_2=580nm

For example:

For Venezuela heavy crude blended with 1% used engine oil,

$D_1 = 0.486$, and $D_2 = 0.355$

$B = (\log 0.486 - \log 0.355)/ 40 \times 10^{-9} = 3.41 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.41 \times 10^6 = 2.755 \times 10^{10}$ and

$d = 6000/939.5 \times 2.755 \times 10^{10} = 2.3181 \times 10^{-10}$m

On this basis, Tables 5.1, 5.6 and 5.11 were formed.

Similar calculations for pure and other blends are shown in Appendix I.

Next is the tabular presentation of the material balance of the fractional cuts from TBP distillation of the pure and blended crude and comparison of the distillate yields in support of the objective of carrying out this research work.

Finally, as yardstick in measuring the pattern of enhancement of the light-ends, the long residues of the crudes and their blends were subjected to AAS analysis for 'freed' d-metals from the porphyrins.

Table 4.1: Spectrophotometric Analysis and the Average Particle Size of Venezuela Heavy Crude Oil and its Blend

UEO Content, %	Absorbance, D		Av. Part. diam, $dx10^{-10}$m	UEO Content, %	Absorbance, D		Av. Part. diam, $dx10^{-10}$m
	λ_1=580nm	λ_2=620nm			λ_1=580nm	λ_2=620nm	
0	0.773	0.501	1.6718	16	0.367	0.264	2.2098
1	0.486	0.355	2.3181	17	0.362	0.259	2.1742
2	0.570	0.409	2.1962	18	0.371	0.264	2.1395
3	0.609	0.440	2.2388	19	0.481	0.345	2.1906
4	0.418	0.299	2.1738	20	0.417	0.300	2.2106
5	0.490	0.354	2.2398	21	0.387	0.267	2.1536
6	0.405	0.287	2.114	22	0.397	0.284	2.1733
7	0.443	0.320	2.2468	23	0.530	0.381	2.2054
8	0.435	0.309	2.1286	24	0.487	0.348	2.1662
9	0.446	0.317	2.1323	25	0.433	0.313	2.2431
10	0.388	0.275	2.1147	26	0.582	0.421	2.248
11	0.496	0.353	2.1404	27	0.515	0.369	2.1837
12	0.397	0.281	2.1065	28	0.521	0.376	2.232
13	0.586	0.421	2.2014	29	0.425	0.304	2.132
14	0.472	0.337	2.1609	30	0.385	0.277	2.2112
15	0.652	0.470	2.2241				

The data from Table 4.1 above was used to plot the graph in Figure 4.1.

As it can be observed in Figure 4.1 and reported by Unger and Andreeva (1995), the pattern of the graph that was obtained is slightly wavelike which confirms the mutual attraction and repulsion of the hydrocarbon components of the micelle (particle size) due to association and dissociation of the molecules when the crude oil samples and various contents of the UEO were blended.

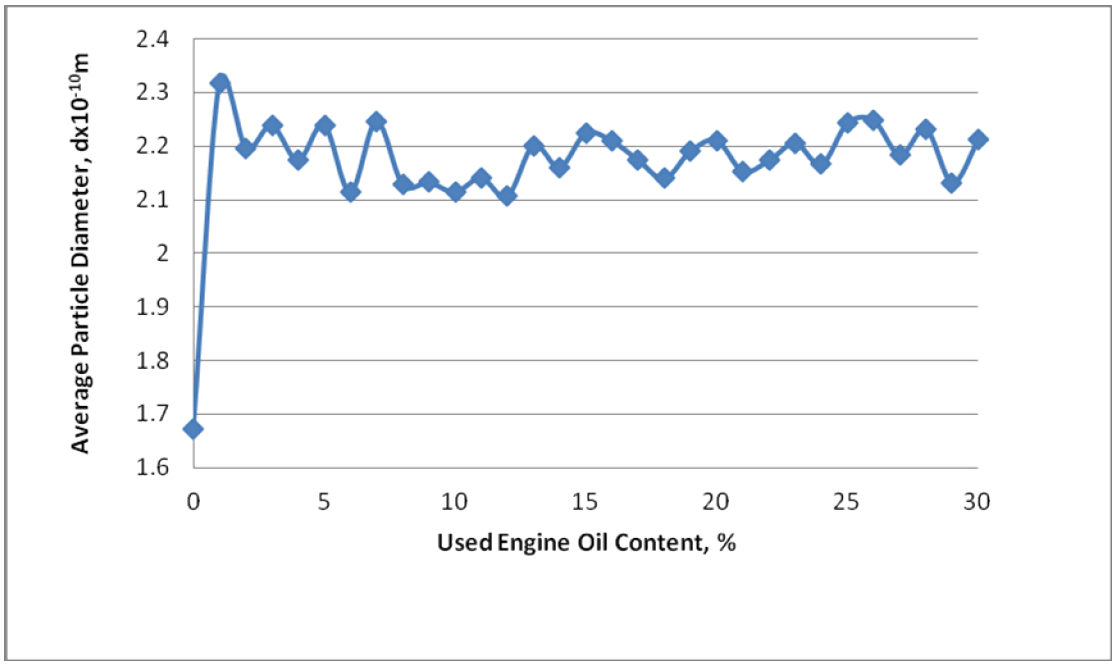


Figure 4.1: Trend of Particle Size of Venezuela Heavy Crude with UEO Blending

The blended points of 1% and 12% on the curve which correspond with the maximum and minimum particle diameters respectively were chosen as basis for carrying out TBP distillation.

The results of the distillation of the pure and blended Venezuela Heavy crude and the various blends with UEO are hereby as given in Tables 4.2, 4.3 and 4.4.

Table 4.2: Material Balance of TBP Distillation of Venezuela Heavy Crude Oil (0%UEO)

Fractional Cut, ^{o}C	Vapour Temperature,		Yield,		Cumulative Wt. %
	^{o}C	^{o}F	(g)	Wt. %	
IBP-120	50	122	0.1725	0.02	0.02
120-180	62	144	42.5780	5.32	5.34
180-240	156	313	53.4320	6.68	12.02
240-360	248	478	147.6960	18.37	30.39
>360	-	-	543.0000	67.88	98.27
Loss	-	-	13.1215	1.73	100.00
Total			800.0000	100.00	-

The graph of Figures 4.2, 4.3 and 4.4 are constructed for comparison with the standard correlation of cumulative percentage yield as a function of vapour temperature.

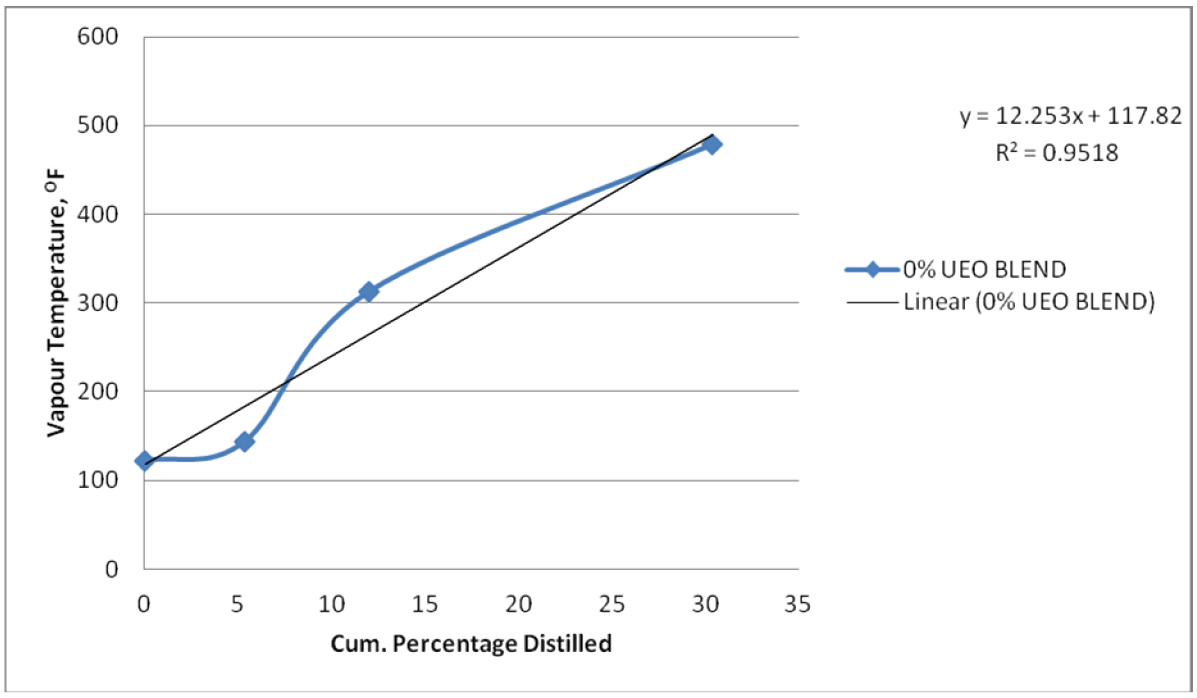


Figure 4.2: Average True Boiling Point Distillation Curve of Light Ends of Venezuela Crude Oil (0% UEO)

Table 4.3: Material Balance of TBP Distillation of Venezuela Heavy Crude Oil Blended with 1%UEO

Fractional Cut, ^{o}C	Vapour Temperature,		Yield,		Cumulative Wt. %
	^{o}C	^{o}F	(g)	Wt. %	
IBP-120	64	147	4.6955	0.59	0.59
120-180	92	198	38.196	4.77	5.36
180-240	152	306	61.633	7.70	13.06
240-360	210	410	153.0461	19.13	32.19
>360	-	-	535.9231	67.00	99.19
Loss	-	-	6.5063	0.81	100.00
Total			800.0000	100.00	

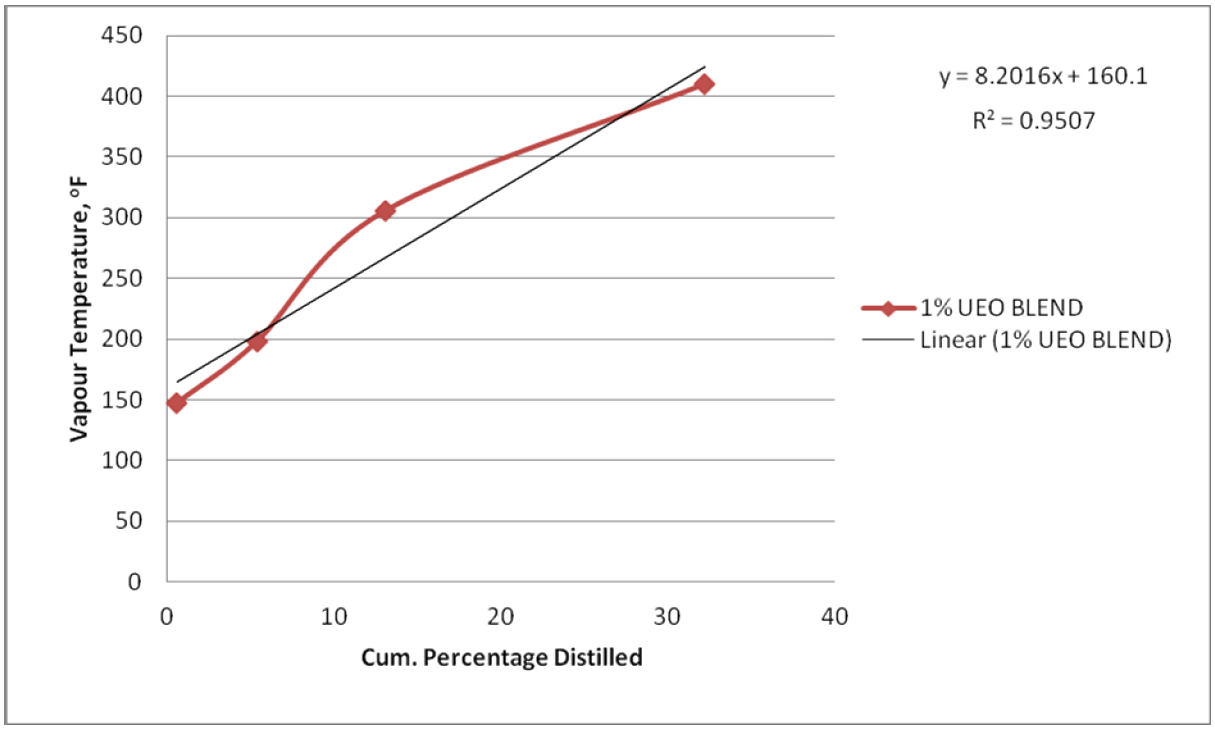


Figure 4.3: Average True Boiling Point Distillation Curve of the Light Ends of Venezuela Crude Oil Blended with 1% UEO

Table 4.4: Material Balance of TBP Distillation of Venezuela Heavy Crude Oil Blended with 12%UEO

Fractional Cut, ^{o}C	Vapour Temperature,		Yield,		Cumulative Wt. %
	^{o}C	^{o}F	(g)	Wt. %	
IBP-120	50	122	0.9439	0.12	0.12
120-180	98	208	42.4816	5.31	5.43
180-240	148	298	61.1744	7.65	13.08
240-360	242	468	144.4729	18.05	31.13
>360	-	-	543.0086	67.88	99.01
Loss	-	-	7.9186	0.99	100.00
Total			800.0000	100.00	

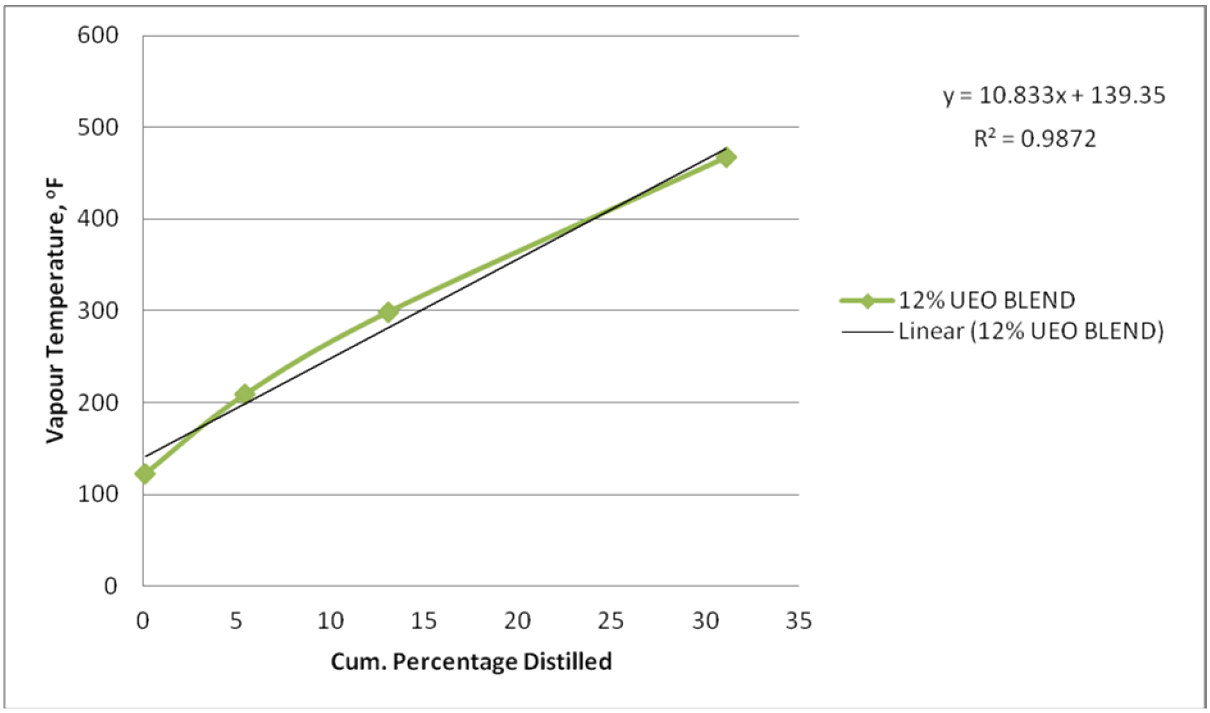


Figure 4.4: Average True Boiling Point Distillation Curve of the Light Ends of Venezuela Crude Oil Blended with 12% UEO

Figure 4.5 below compares the distillates that were obtained from the TBP distillation of the Pure crude and their various blends with UEO.

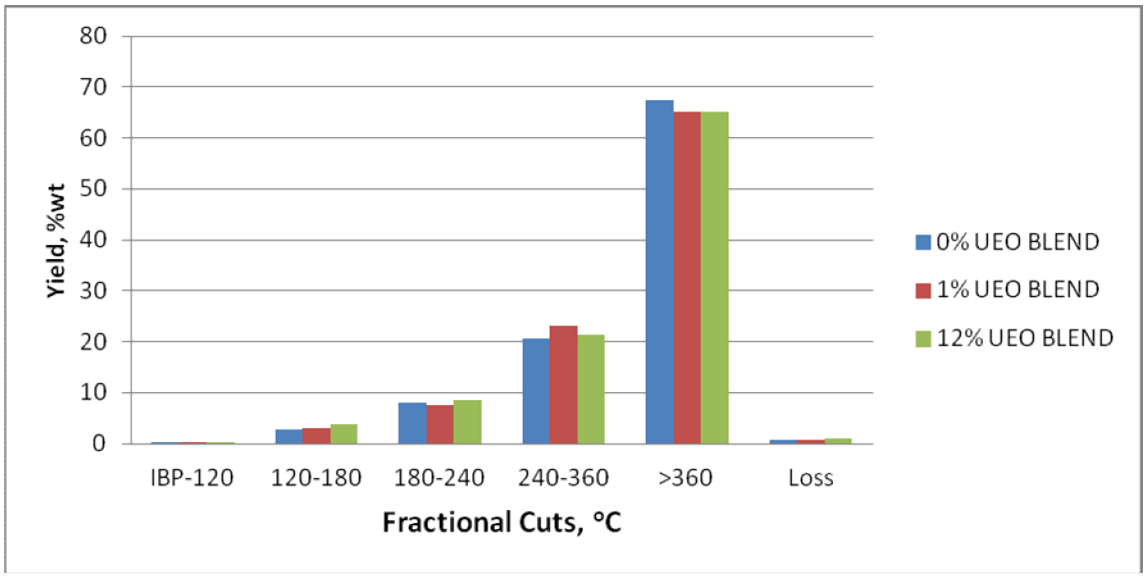


Figure 4.5: Comparison of Yields of Pure Venezuela Heavy Crude and Various Blends with UEO

In tabular form Figure 4.5 can be transformed into data as in Table 4.5.

Table 4.5: Comparison of the Yields of Fractional Cuts of Venezuela Heavy Crude and the Various Blends

Fractional Cuts, °C	Pure Crude (0% Blend)	Change in Yields, %			
		For 1% Blend of UEO	Enhancement (+/-)	For 12% Blend of UEO	Enhancement (+/-)
IBP-120	0.02	0.59	+0.57	0.12	+0.10
120-180	5.32	4.77	-0.55	5.31	-0.01
180-240	6.68	7.70	+1.02	7.65	+0.97
240-360	18.37	19.13	+0.76	18.05	-0.32
Sub-total	30.39	32.19	+1.80	31.13	+0.74
>360	67.88	67.00	-0.88	67.88	+0.00
Loss	1.73	0.81	-0.92	0.99	-0.74
Sub-total	69.61	67.81	-1.80	68.87	-0.74
Grand total	100.00	100.00	0.00	100.00	0.00

Table 4.6: Spectrophotometric Analysis and the Average Particle Size of Mixed (50%Venezuela:50% Antan wt.) Heavy Crude Oil and its Blend with UEO

UEO Content, %	Absorbance, D		Av. Part diam, $dx10^{-10}m$	UEO Content, %	Absorbance, D		Av. Part diam, $dx10^{-10}m$
	λ_1=580nm	λ_2=620nm			λ_1=580nm	λ_2=620nm	
0	0.518	0.431	2.0800	16	0.349	0.257	2.3734
1	0.445	0.317	2.1412	17	0.252	0.179	2.1234
2	0.391	0.278	2.1293	18	0.278	0.200	2.2055
3	0.365	0.260	2.1410	19	0.305	0.219	2.1926
4	0.343	0.243	2.1100	20	0.409	0.293	2.1775
5	0.429	0.305	2.1917	21	0.357	0.256	2.1839
6	0.418	0.297	2.1252	22	0.326	0.234	2.1904
7	0.330	0.240	2.2807	23	0.338	0.246	2.2221
8	0.450	0.322	2.1699	24	0.217	0.159	2.3354
9	0.375	0.268	2.1620	25	0.386	0.277	2.1888
10	0.459	0.330	2.2011	26	0.347	0.248	2.1622
11	0.322	0.231	2.1867	27	0.357	0.256	2.1839
12	0.282	0.202	2.1768	28	0.366	0.263	2.1976
13	0.341	0.244	2.1698	29	0.305	0.219	2.1926
14	0.368	0.262	2.1377	30	0.249	0.177	2.1279
15	0.306	0.220	2.2011				

The data from Table 4.6 above was used to plot the graph in Figure 4.6.

The pattern of the graph in Figure 4.6 is similar to the one as obtained in Figure 4.1. The explanation for this kind of behavior has been adequately covered in that section of the result.

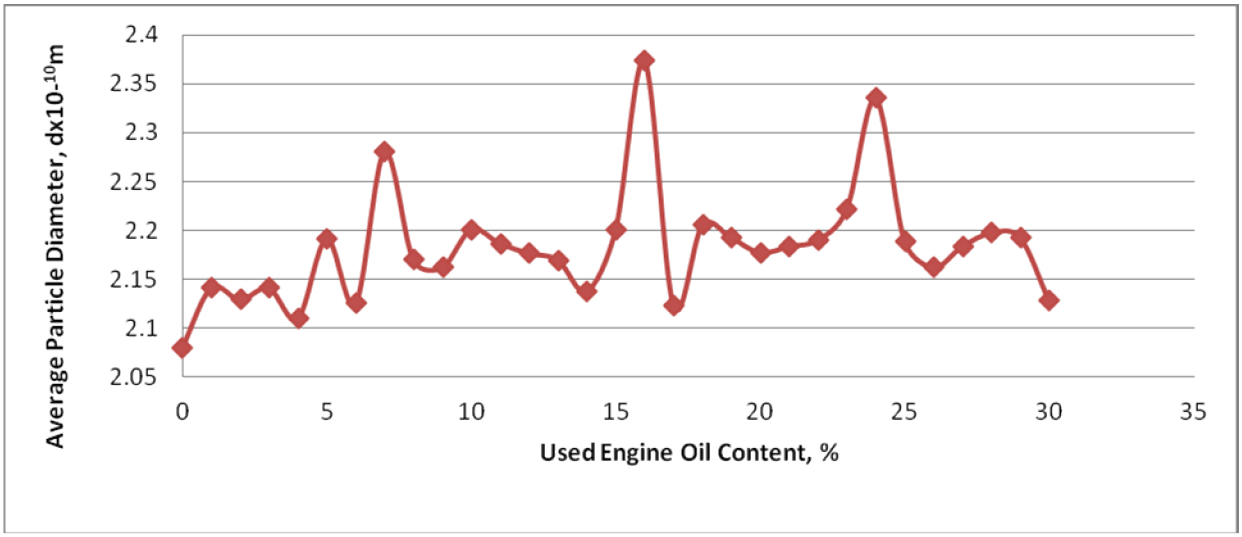


Figure 4.6: Trend of Particle Size of Mixed Heavy Crude with UEO Blending

Similarly, the blended points of 16% and 4% on the curve which corresponded with the maximum and minimum particle diameters respectively were chosen as basis for carrying out TBP distillation.

The results of the distillation of pure mixed heavy and various blends with UEO are as given in Tables 4.7, 4.8 and 4.9.

Table 4.7: Material Balance of TBP Distillation of Mixed Heavy Crude Oil (0%UEO)

Fractional Cut, ^{o}C	Vapour Temperature,		Yield,		Cumulative Wt. %
	^{o}C	^{o}F	(g)	Wt. %	
IBP-120	48	118	0.2648	0.03	0.03
120-180	85	185	22.3270	2.79	2.82
180-240	139	282	64.4020	8.05	10.87
240-360	252	486	165.5300	20.69	31.56
>360	-	-	540.3302	67.55	99.11
Loss	-	-	7.1460	0.89	100.00
Total			800.0000	100.00	

The plots in Figures 4.7, 4.8 and 4.9 are similarly constructed for comparison with the standard correlation of cumulative percentage yield as a function of vapour temperature.

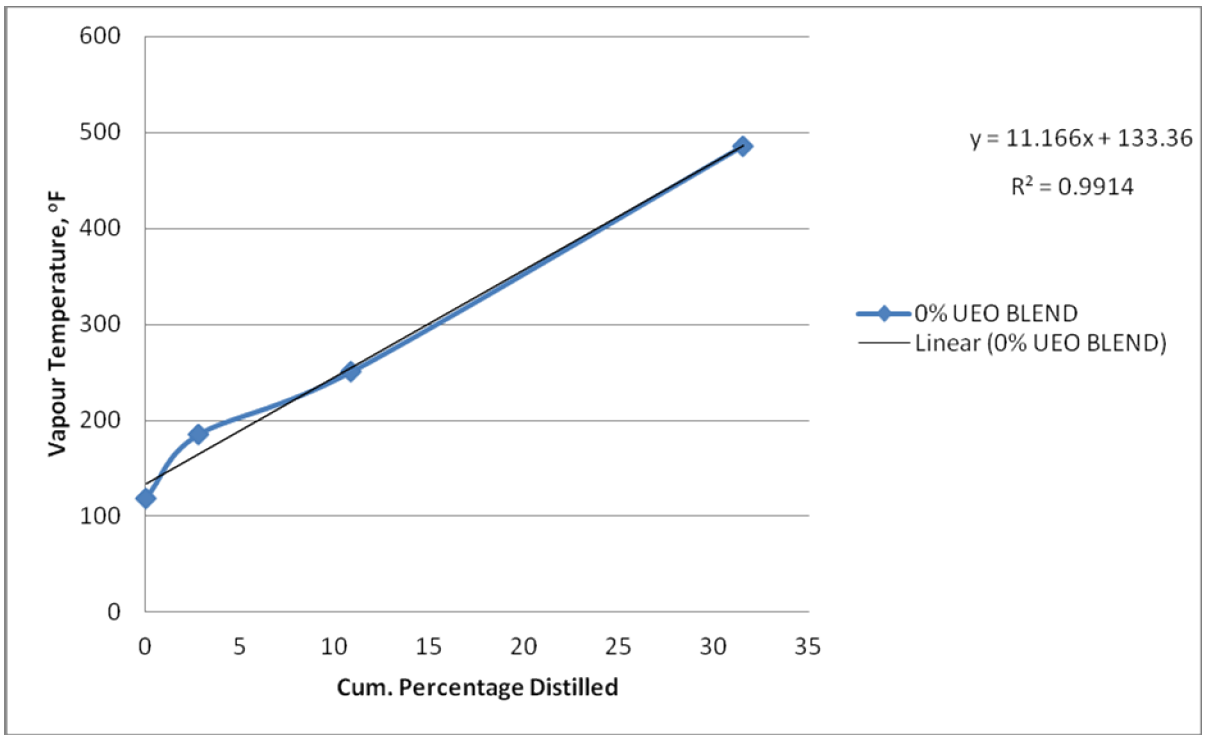


Figure 4.7: Average True Boiling Point Distillation Curve of the Light Ends of Mixed Crude Oil (0% UEO)

Table 4.8: Material Balance of TBP Distillation of Mixed Heavy Crude Oil Blended with 16% UEO

Fractional Cut, °C	Vapour Temperature,		Yield,		Cumulative Wt. %
	°C	°F	(g)	Wt. %	
IBP-120	56	132.8	0.2210	0.03	0.03
120-180	88	190.4	23.8428	2.98	3.01
180-240	145	293	60.8380	7.60	10.61
240-360	244	471.2	186.2220	23.28	33.89
>360	-	-	522.2031	65.28	99.17
Loss	-	-	6.6731	0.83	100.00
Total			800.0000	100.00	

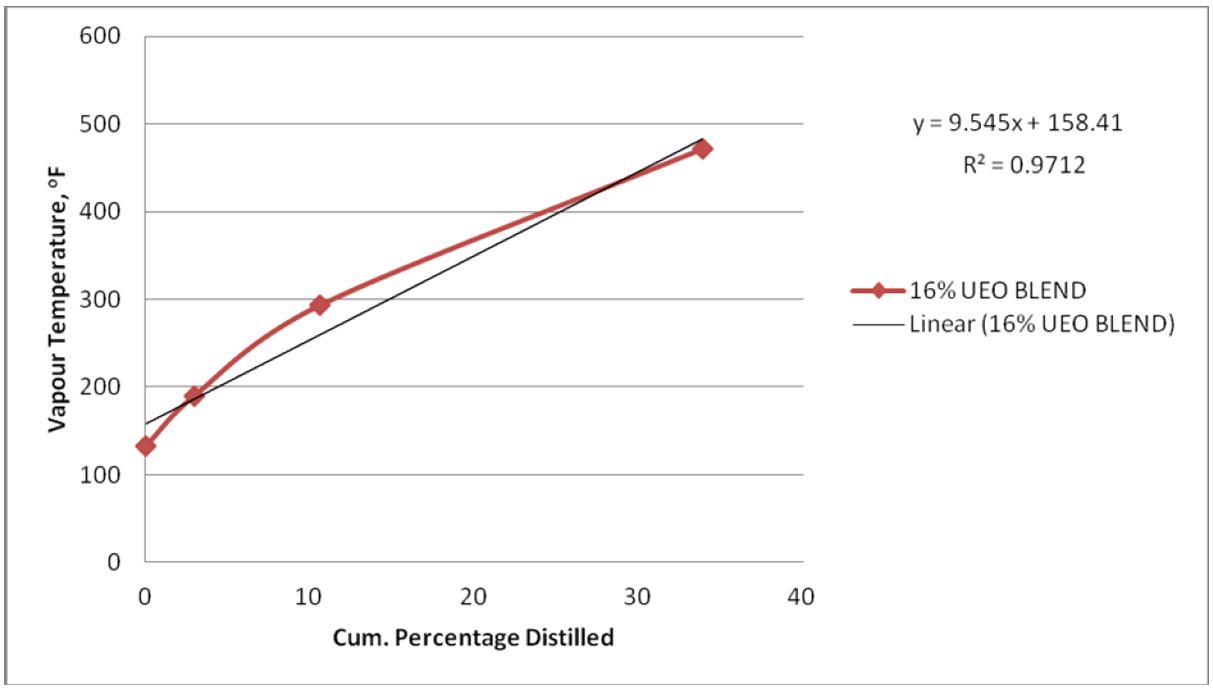


Figure 4.8: Average True Boiling Point Distillation Curve of the Light Ends of Mixed Crude Oil Blended with 16% UEO

Table 4.9: Material Balance of TBP Distillation of Mixed Heavy Crude Oil Blended with 4% UEO

Fractional Cut, °C	Vapour Temperature,		Yield,		Cumulative Wt. %
	°C	°F	(g)	Wt. %	
IBP-120	52	126	1.0028	0.13	0.13
120-180	90	194	29.3618	3.67	3.80
180-240	147	297	69.4800	8.68	12.48
240-360	248	478	170.6590	21.33	33.81
>360	-	-	521.2557	65.16	98.97
Loss	-	-	8.2411	1.03	100.00
Total			800.0000	100.00	

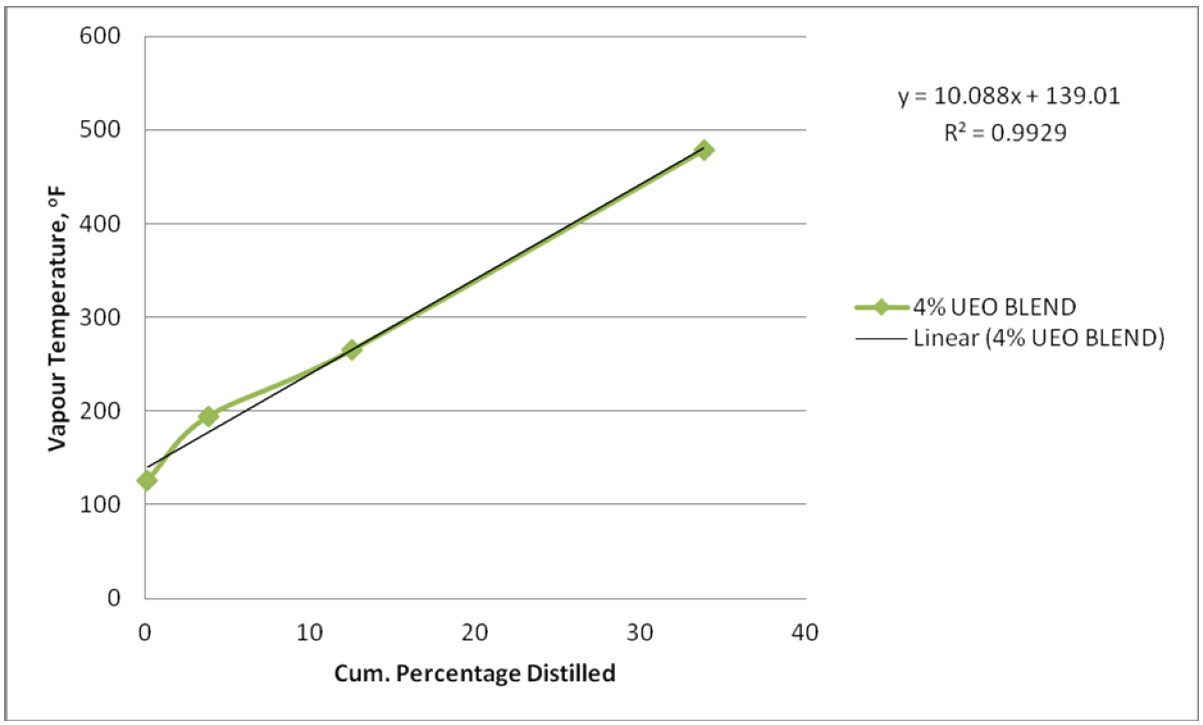


Figure 4.9: Average True Boiling Point Distillation Curve of the Light Ends of Mixed Crude Oil Blended with 4% UEO

Figure 4.10 below compares the products that are obtained from the TBP distillation of the Pure and the various blends.

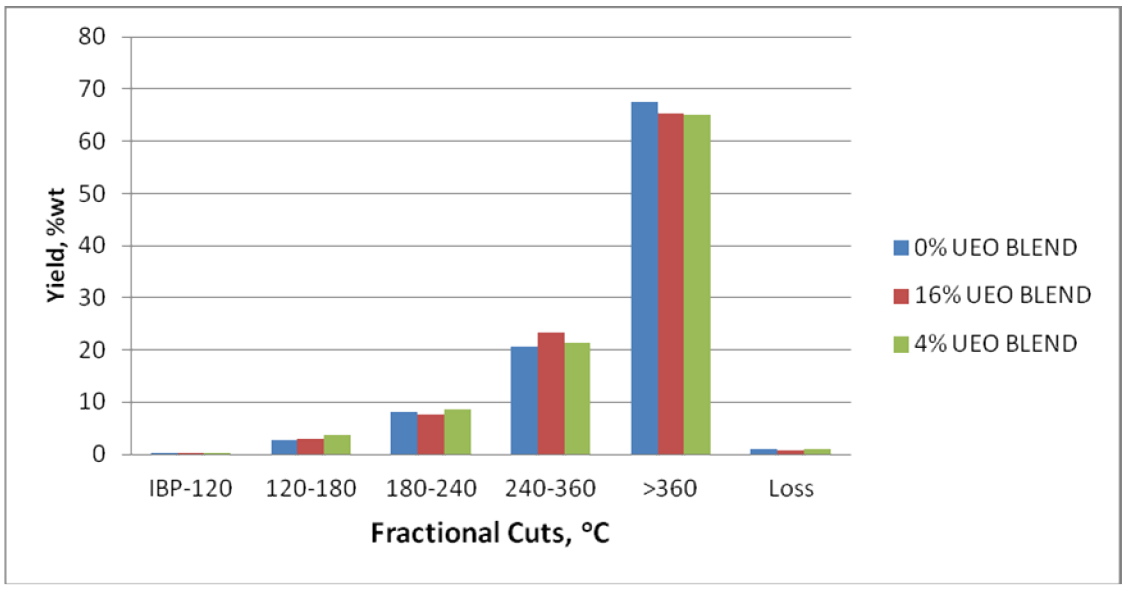


Figure 4.10: Comparison of Yields of Mixed Heavy Crude and Various Blends with UEO

In tabular form Figure 4.10 can be transformed into Table 4.10.

Table 4.10: Comparison of the Yields of Fractional Cuts of Mixed Heavy Crude and the Various Blends

Fractional Cuts, ^{o}C	Pure Crude (0% Blend)	Change in Yields, %			
		For 16% Blend of UEO	Enhancement (+/-)	For 4% Blend of UEO	Enhancement (+/-)
IBP-120	0.03	0.03	0.00	0.13	+0.10
120-180	2.79	2.98	+0.19	3.67	+0.88
180-240	8.05	7.60	-0.45	8.68	+0.63
240-360	20.69	23.28	+2.59	21.33	+0.64
Sub-total	31.56	33.89	+2.33	33.81	+2.25
>360 ^{o}C	67.55	65.28	-2.27	65.16	-2.38
Loss	0.89	0.83	-0.06	1.03	+0.14
Sub-total	68.44	66.11	-2.33	66.19	-2.25
Grand total	100.00	100.00	0.00	100.00	0.00

Table 4.11: Spectrophotometric Analysis and the Average Particle Size of Antan Heavy Crude Oil and its Blends

UEO Content, %	Absorbance, D		Av. Part. diam, $dx10^{-10}m$	UEO Content, %	Absorbance, D		Av. Part. diam, $dx10^{-10}m$
	λ_1=580nm	λ_2=620nm			λ_1=580nm	λ_2=620nm	
0	0.988	0.702	2.216	16	0.665	0.493	2.532
1	0.957	0.715	2.599	17	0.704	0.527	2.616
2	0.789	0.591	2.622	18	0.666	0.492	2.501
3	0.863	0.659	2.800	19	0.171	0.153	7.385
4	0.833	0.623	2.606	20	0.676	0.505	2.598
5	0.888	0.668	2.660	21	0.624	0.461	2.503
6	0.788	0.589	2.603	22	0.138	0.123	6.580
7	0.708	0.520	2.454	23	0.916	0.753	3.864
8	0.795	0.587	2.508	24	0.752	0.568	2.702
9	0.775	0.589	2.760	25	0.790	0.596	2.690
10	0.764	0.574	2.648	26	0.140	0.123	5.850
11	0.282	0.236	4.26	27	0.475	0.354	2.580
12	0.753	0.568	2.688	28	0.712	0.538	2.704
13	0.778	0.589	2.72	29	0.641	0.489	2.804
14	0.187	0.165	6.054	30	0.669	0.508	2.752
15	0.802	0.604	2.672				

The data from Table 4.11 above was used to plot the graph in Figure 4.11.

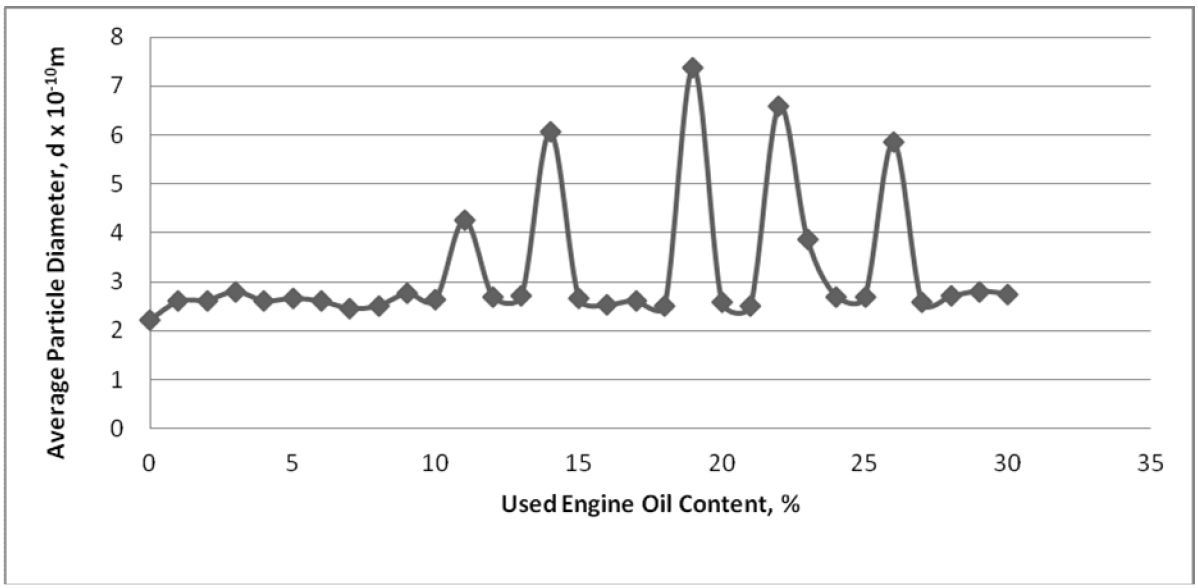


Figure 4.11: Trend of Particle Size of Antan Heavy Crude with UEO Blending

Just like in Figures 4.1 and 4.6, the blended points of 19% and 7% on the curve which correspond with the maximum and minimum particle diameters respectively were chosen as basis for carrying out TBP distillation.

The results of the distillation of pure Antan heavy and various blends with UEO are as given in Tables 4.12, 4.13 and 4.14.

Table 4.12: Material Balance of TBP Distillation of Antan Heavy Crude Oil (0%UEO)

Fractional Cut, ^{o}C	Vapour Temperature,		Yield,		Cumulative Wt. %
	^{o}C	^{o}F	(g)	Wt. %	
IBP-120	54	129	0.0000	0.00	0.00
120-180	94	201	78.3600	9.80	9.80
180-240	120	248	87.5146	10.93	20.73
240-360	232	450	110.2276	13.78	34.51
>360	-	-	508.5455	63.57	98.08
Loss	-	-	15.3523	1.92	100.00
Total			800.0000	100.00	

Just like before, the graph of Figures 4.12, 4.13 and 4.14 are constructed for comparison with the standard correlation of cumulative percentage yield as a function of vapour temperature.

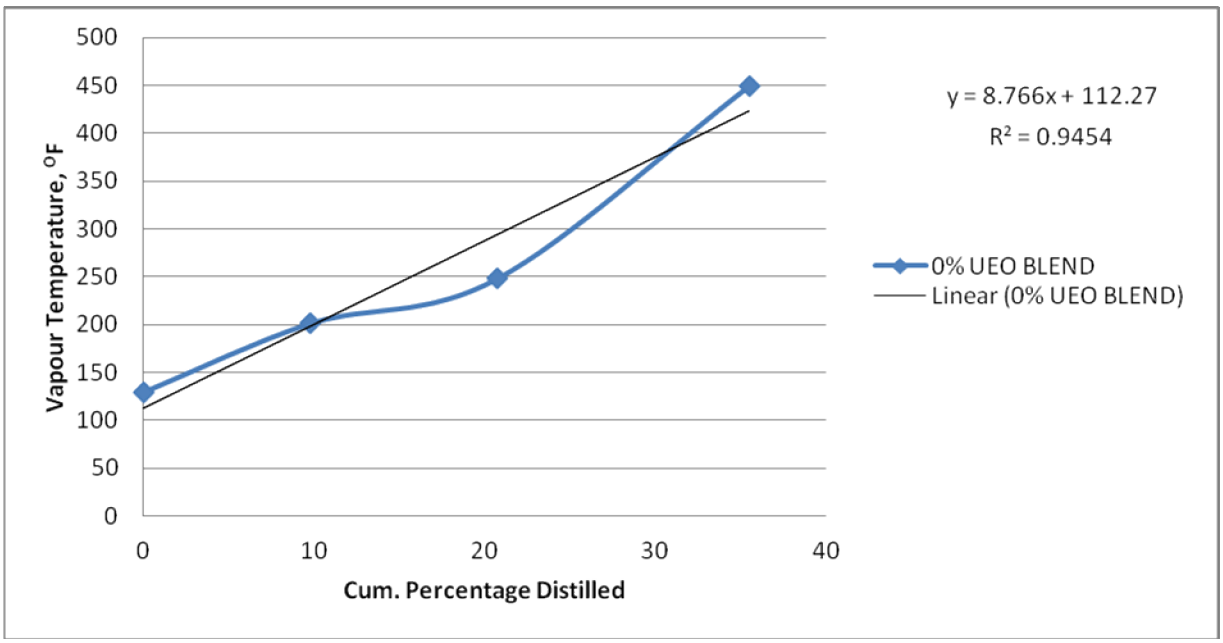


Figure 4.12: Average True Boiling Point Distillation Curve of the Light Ends of Antan Crude Oil (0% UEO)

Table 4.13: Material Balance of TBP Distillation of Antan Heavy Crude Oil Blended with 19% UEO

Fractional Cut, °C	Vapour Temperature,		Yield,		Cumulative Wt. %
	°C	°F	(g)	Wt. %	
IBP-120	60	140	0.0000	0.00	0.00
120-180	79	174	71.4497	8.93	8.93
180-240	138	280	121.4291	15.18	24.11
240-360	242	468	142.5661	17.82	41.93
>360	-	-	447.6527	55.96	97.89
Loss	-	-	16.9024	2.11	100.00
Total			800.0000	100.00	

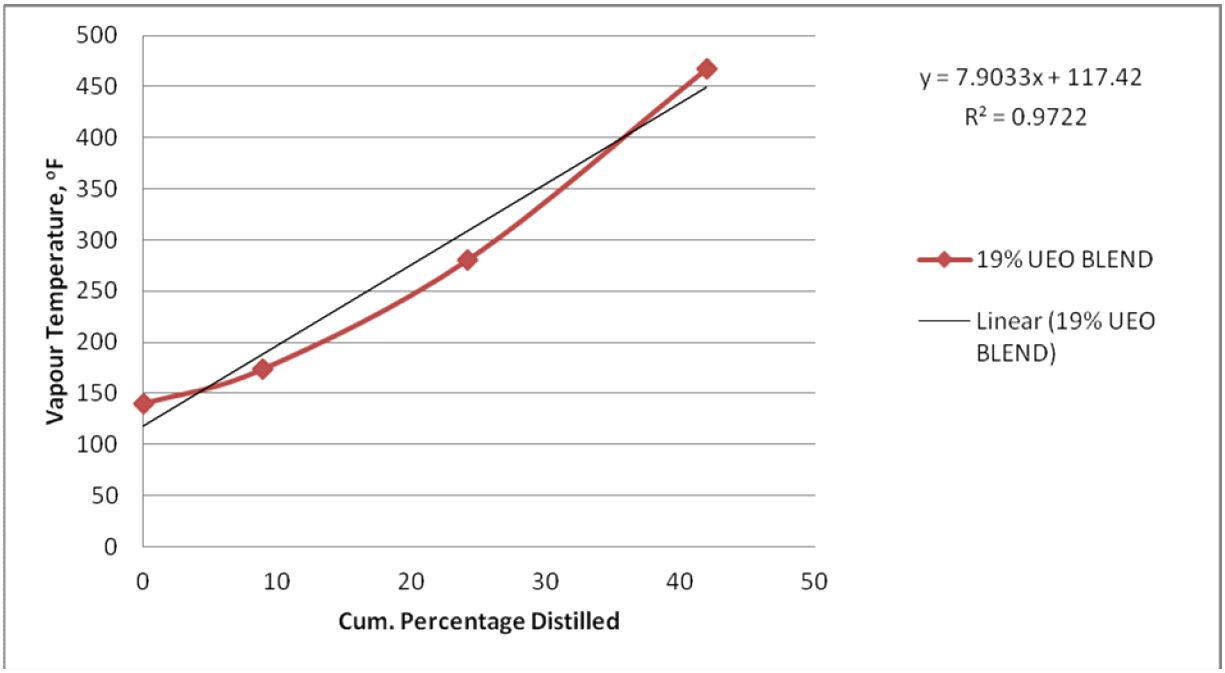


Figure 4.13: Average True Boiling Point Distillation Curve of the Light Ends of Antan Heavy Crude Oil Blended with 19% UEO

Table 4.14: Material Balance of TBP Distillation of Antan Heavy Crude Oil Blended with 7%UEO

Fractional Cut, °C	Vapour Temperature,		Yield,		Cumulative Wt. %
	°C	°F	(g)	Wt. %	
IBP-120	62	144	0.0000	0.00	0.00
120-180	92	198	79.8743	9.98	9.98
180-240	119	246	83.9252	10.49	20.47
240-360	264	507	126.3749	15.80	36.27
>360	-	-	493.5771	61.70	97.97
Loss	-	-	16.2485	2.03	100.00
Total			800.0000	100.00	

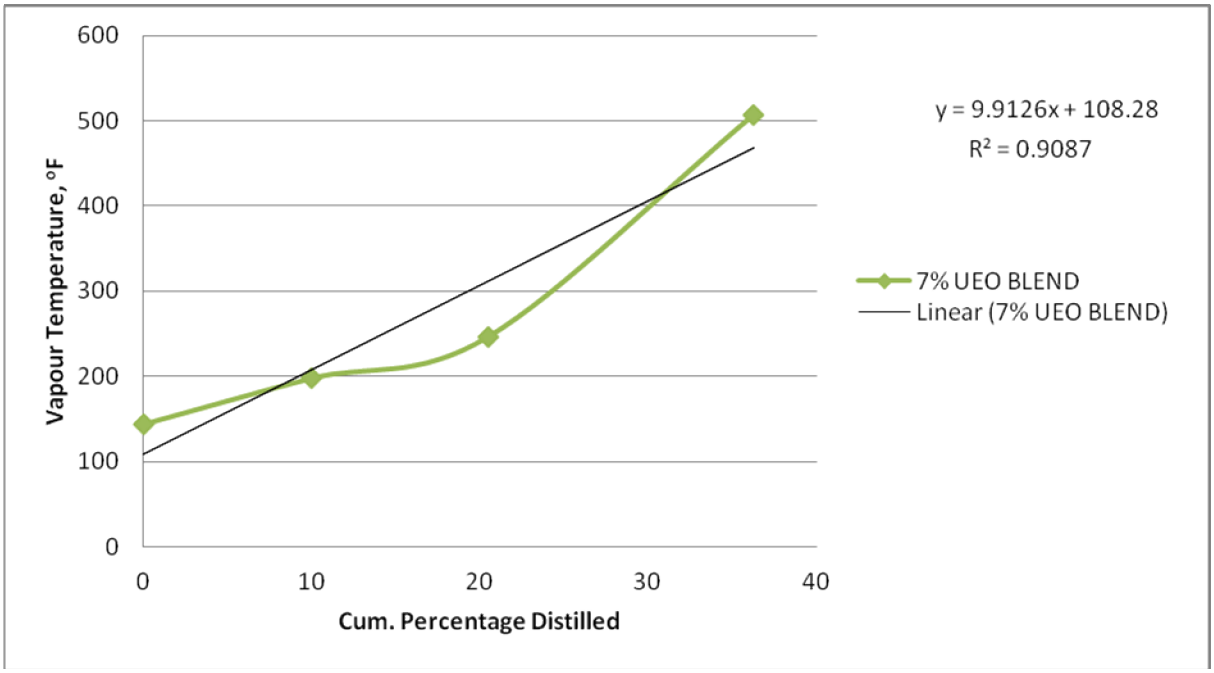


Figure 4.14: Average True Boiling Point Distillation Curve of the Light Ends of Antan Crude Oil Blended with 7% UEO

Figure 4.15 below compares the products that are obtained from the TBP distillation of the Pure and the various blends.

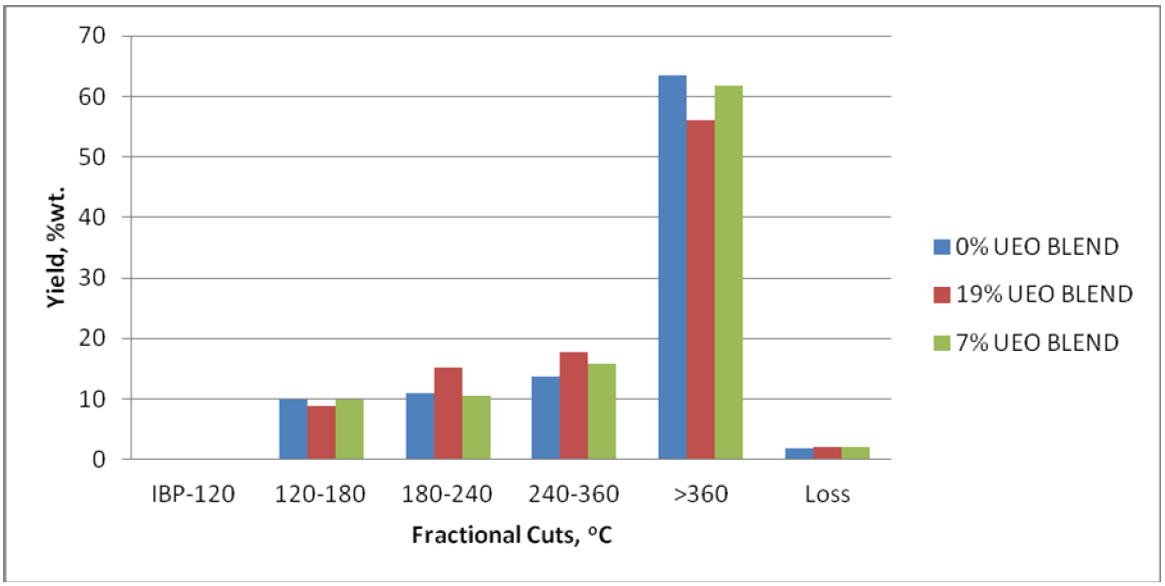


Figure 4.15: Comparison of Yields of Antan Heavy Crude and Various Blends with UEO

In tabular form Figure 4.15 is transformed into Table 4.15.

Table 4.15: Comparison of the Yields of Fractional Cuts of Antan Heavy Crude and the Various Blends

Fractional Cuts, ^{o}C	Pure Crude (0% Blend)	Change in Yields, %			
		For 19% Blend of UEO	Enhancement (+/-)	For 7% Blend of UEO	Enhancement (+/-)
IBP-120	0.00	0.00	0.00	0.00	0.00
120-180	9.80	8.93	-0.86	9.98	+0.18
180-240	10.93	15.18	+4.25	10.49	-0.44
240-360	13.78	17.82	+4.04	15.80	+2.02
Sub-total	34.51	41.93	+7.42	36.27	+1.76
>360	63.57	55.96	-7.61	61.70	-1.87
Loss	1.92	2.11	+0.19	2.03	+0.11
Sub-total	65.49	58.07	-7.42	63.73	-1.76
Grand total	100.00	100.00	0.00	100.00	0.00

AAS Analysis of the Residue

The sets of data that were analyzed are fractional cuts (>360^{o}C) which were obtained from TBP distillation of all the pure crudes and their various blends are as shown in Tables 4.2, 4.3, 4,4, 4.7, 4.8, 4.9, 4.12, 4.13 and 4.14. This is because it is these fractional cuts that contained the various 3d-metals (vanadium, nickel, cobalt, iron, etc) that were freed from porphyrins during the unavoidable cracking in the process of distillation. As earlier stated it can be speculated that it's these intermittent free radicals that were generated from porphyrins and some other organometalic compounds that regrouped into various structures and contributed to the formation of new products (lighter-ends and cokes). This is how the light ends were enhanced as reflected in the research work.

As earlier pointed out too, the most suitable form of analysis to determine these free radicals and the d-metals that form ligands in porphyrins is through electron paramagnetic resonance (EPR) spectroscopy. However, in the absence of EPR spectroscopy, atomic absorption spectroscopy (AAS) was used as an optional replacement. This is because while the former is more specific in the analysis of porphyrins the latter cannot be used at all. Nevertheless, the

metals detected by the use of AAS is in quantity, a reflection of how much porphyrins that was initially present in the long residue i.e. fractional cuts (>360^{o}C) (Ajinomoh, 2005). This is the reason why an option of AAS analysis was considered for the research work.

The results of the AAS analysis of the long residue of pure Venezuela crude, Mixed crude, Antan crude and their various blends which were carried out in the Research and Development unit of NNPC, Port Harcourt are presented in Table 4.16.

Table 4.16: AAS Analyses Report of Pure Venezuela Crude, Mixed Crude, Antan Crude and the Various Blends

S/No.	Sample Description	Fe (ASTM D1068), ppm	Ni (ASTM D1886), ppm	V (ASTM D3373), ppm
Fractional cut (>360^{o}C) of Venezuela Crude				
1	0% UEO Blend	2.3	4.7	< 0.01
2	1% UEO Blend	2.8	11.1	< 0.01
3	12% UEO Blend	7.3	12.0	< 0.01
	Fractional cut (>360^{o}C) of Mixed Crude			
1	0% UEO Blend	9.4	13.7	< 0.01
2	16% UEO Blend	13.5	21.5	< 0.01
3	4% UEO Blend	14.3	26.2	< 0.01
Fractional cut (>360^{o}C) of Antan Crude				
1	0% UEO Blend	16.5	22.7	< 0.01
2	19% UEO Blend	23.1	33.6	< 0.01
3	7% UEO Blend	17.4	40.3	< 0.01

4.2 **DISCUSSION OF RESULTS**

In this section, most of the sets of data (Charts and Tables) that were generated in the cause of carrying out this research work are discussed. The results and/or problems would be interpreted by trying to speculate it in terms of cause and effect phenomenon.

4.2.1 Average Particle Diameter of the Blends

For the blended Venezuela heavy crude, it varies from minimum value of 2.1065×10^{-10}m (12% UEO blend) to a maximum value of 2.3255×10^{-10}m (1% UEO blend), while the rest of the values fall between these two extremes as shown in Table 4.1 and Figure 4.1. In case of blended Mixed heavy crude, it varies from minimum value of 2.11×10^{-10}m (4% UEO blend) to a maximum value of 2.3734×10^{-10}m (16% UEO blend), while the rest of the values fall between these two extremes as shown in Table 4.6 and Figure 4.6. Finally, for the blended Antan heavy crude, it varies from a minimum value of 2.454×10^{-10}m (7% UEO blend) to maximum value of 7.385×10^{-10}m (19% UEO blend), while again the rest of the values fall between these two extremes as shown in Table 4.11 and Figure 4.11. The generated data depicts that the average particle sizes of the blends except for that of Venezuela heavy crude to some certain degree are very unstable. The behavior exhibited and shown in Figures 4.1, 4.6 and 4.11 are due to the mutual attractions and repulsions of the hydrocarbon constituents (aliphatic, mono- and polycyclic benzene) of the individual system (i.e. crude oil and the UEO) (Unger and Andreeva, 1995). In case of Venezuela heavy crude, the relative stability is explained on the account that at some certain ratios the attraction and repulsion forces of the hydrocarbon constituents of the system are fairly close and that when it can no longer maintain it at another ratio, the diameter may decrease or increase in size.

However, the major reason for choosing these two extreme points for TBP distillation exercise according to Safieva (1998) is that they act as guide for maximum or minimum enhancement of light ends recovery during distillation process. In this work, higher enhancement of light ends is tilted towards larger particle diameters, which is contrary to what had been reported by some prominent investigators like Sunyaev *et al* (1990) and Mohammed (2001) in a

similar work. However this may be attributed to lesser attractive forces between individual molecules that constitute the CDU of the blends by the time UEO samples were added. Of course this is quite in agreement with what Belousov and Bushueva (1987) reported on molecular association and dissociation of the components of crude oil especially when subjected to external influences such as temperature, pressure, blending, etc. Thus, blending of crude oil samples with UEO has brought about lesser attractive forces between individual hydrocarbon components that constitute the micelle thereby resulting into larger particle size and correspondingly the higher light ends recovery when compared with smaller sizes as reported in the outcome of this research work.

4.2.2 TBP Distillation of the Pure and Blended Crude Oils

The enhanced recovery of light-ends (<360^{o}C fractional cuts) for Venezuela heavy crude is 1.8% wt. and 0.74% wt. for the chosen maximum and minimum particle diameter respectively, while that of Mixed heavy crude was 2.33% wt. and 2.25% wt. for the maximum and minimum particle diameter respectively and finally, Antan heavy crude's recovery enhancement was 7.42wt. and 1.76% wt. for the maximum and minimum particle diameter respectively. Saidakhmedov *et al* (1986) and Mohammed (2001) reported that the difference between the potential yield of light fractions distilling below 350^{o}C and the actual yields of total light products in atmospheric pipestill units may be as great as 5-7% by weight on crude, depending on the quality of that crude, CDU state and solvency of additives being used as blend. The values of enhancements in this work are quite in agreement with what was expected.

4.2.3 Positive and Negative Enhancements

Across the various Tables of 4.5, 4.10 and 4.15 was encountered mostly positive and few negative enhancement values of the fractional cuts. As earlier stated this should not be too strange, because in this research work, it was discussed that the recovery enhancement is not entirely a physical phenomenon, but as well related to a thermal process. Bjorseth (1983), Dias (1987 and 1988) reported asphaltenes decomposition process in heavy crude oils and according to them this unavoidable thermal reaction can result into the formation of more lighter ends and coke products. Of importance too, to mention is the fact that the thermal reaction mechanisms is difficult to establish (Speight, 1999) and as such underscored the reason why any definite trend on their contribution to light ends recovery cannot be predicted.

It must be also stated that some losses of the products were reported across all the Tables in these Sections. Erikh *et al* (1988) revealed that these losses are partially related to light hydrocarbon gases that could not be trapped within the limit of construction of most TBP distillation apparatus and some due to leakages from joints.

4.2.4 Average True Boiling Point Distillation Curves

The slopes of all the graphs fall between the ranges of 7.903 and 12.253vapour temperature/cumulative percent distilled and the intercepts in the range of between 108.28 to 160.1 vapour temperatures (see Figures 4.2, 4.3, 4.4, 4.7, 4.8, 4.9, 4.12, 4.13 and 4.14). Of course, the higher the intercept, the higher the initial boiling point of either the pure crude or the blend and the vice versa.

However, all the sets of data obtained strongly confirmed that the efficiency of the TBP distillation apparatus as fabricated by the author is very high (Nelson, 1958).

4.2.5 Data Analysis

Across Table 4.16, it will be observed that the pure crudes have lesser concentration of the metals that were analysed, which is an indication that the porphyrins and/or other related organometallic compounds were cracked and contributed to the haphazard enhancement of the light ends during the distillation process.

However, what was not established in the research work is the correlation between the concentration of these same metals and the degree of enhancement. Yasuhiro *et al* (2000) and Ajinomoh (2005) reported a novel demetallation process for vanadyl and nickelporphyrins from petroleum residue by photochemical reaction (UV rays). In essence any form of demetallation exercise which in this case asphalthene or porphyrin (d-metals complexes like cobalt, chromium, copper, manganese, titanium, etc) decomposition will result in the formation of light ends and stable d-metals as reported in the outcome of the analyses (Quirke, 1987).

Similarly, by going through the Table, it can be reported that all the crudes and their various blends had little or no vanadyl complexes because the concentration of vanadium was very low (<0.01).

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Within the limits of experimental error(s), the following conclusions can be made:

1. Enhancement of the light-ends as a result of blending heavy crude oils with used engine oil through distillation process was achieved. This recovery of light-ends for Venezuela heavy crude was 1.8% wt. and 0.74% wt. for the chosen maximum and minimum particle diameter respectively, while that of Mixed heavy crude was 2.33% wt. and 2.25% wt. for the maximum and minimum particle diameter respectively and finally, Antan heavy crude's recovery enhancement was at 7.42% wt. and 1.76% wt. for the maximum and minimum particle diameter respectively. Most of the reported cases of enhancement of light ends by using the same method were in the range of 2-7% by weight on the crude.
2. The influence of particle sizes of the pure and blended crudes on the outcome of the light ends cannot be overemphasized. For the blended Venezuela heavy crude, it varies from minimum value of 2.1065×10^{-10}m (12% UEO blend) to a maximum value of 2.3255×10^{-10}m (1% UEO blend), in case of blended Mixed heavy crude, it varies from minimum value of 2.11×10^{-10}m (4% UEO blend) to a maximum value of 2.3734×10^{-10}m (16% UEO blend), and finally, for the blended Antan heavy crude, it varies from a minimum value of 2.454×10^{-10}m (7% UEO blend) to maximum value of 7.385×10^{-10}m (19% UEO blend). Within the limit of this work, these confirmed that the larger the particle size blend the higher the chance of higher light-ends recovery.
3. The role of porphyrins (d-metals hydrocarbon complexes) towards the enhancement of the light was equally established. This is perhaps because porphyrins or better still

asphaltenes, are thermally unstable in the temperature ranges of which many refining processes are carried out, and as such their cracking may be blessing in disguise to light ends enhancement for many heavy crude oils distillation processes.

4. Influence of particle size of the blends cannot be used to predict the pattern of distribution of the product slate. It would have been expected that after conducting the spectrophotometric analyses of the blends, that should have been enough to establish across, the overall increment or decrement of the whole product slates. Unfortunately this is not so. It is still expected that TBP distillation analysis must be carried out for final outcome of product distribution. This can be laborious and time consuming and thereby making the whole idea of the work less justifying.
5. Based on the slopes which ranged from 7.903 to 12.25vapour temperature/cumulative percent distilled and the intercepts in the range of between 112.27 to 160.1 vapour temperature generated for the average True Boiling Point Distillation Curves of the light ends of all the various samples of pure crudes and their blends, the sets of data that were generated by the TBP distillation apparatus were reliable.

5.1.1 Contribution to Knowledge

Within the limit and scope of this work the following learning outcomes are believed to be the contribution to knowledge that was realized after embarking on this research work:

- Enhancement of light ends from heavy crude oils (Venezuela, Mixed and Antan) using UEO as blends.
- Strong relationship between particle size distribution (crude oil micelle) and the prediction of the level of enhancement.
- The role of d-metal complexes towards the enhancement of the light ends was equally established.

5.2 RECOMMENDATIONS

1. It looks more probable that instead of calculating the particle diameter of the blends, other direct measurement using sub-particle bombardment for more accurate data generation could be employed.
2. The role of other stable compounds and ions like I^-, Br^-, OH^-, H_2O, NH_3, NO_2, etc as well as other d-metals in the porphyrin as they might have been liberated during the enhancement of the light-ends should be investigated.
3. The loss encountered in each of the TBP distillation of either the pure crude or the blends should be contained to account for the hydrocarbon gases that are associated with the products.
4. Since porphyrins were suspected to have broken down during the distillation process, enrichment of the fractional cuts with more aromatic hydrocarbon compounds should as well be investigated. This is to establish whether there will be a need to dearomatise naphtha and kerosene fractional cuts during their treatment processes.
5. Though uneconomical, higher ratio of the UEO to the crude almost up to infinite dilution should as well be investigated for higher distillate yield.
6. Higher contact time between UEO and the heavy crude oil should be investigated too.
7. More work should be done at vacuum condition of distillation to establish whether the vacuum distillates are too, enhanced and equally this haphazard pattern of distribution of the products slate is extended to them.
8. Other unconventional crude oils of lower API gravity should be investigated using this approach. This will enhance their patronage as fuel sources at local and global level, thereby justifying their economic potentials.

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Calculation of the Average Particle Size of the Various Blends

Given Data

Density of Venezuela Heavy Crude,

$$\rho_4^{20} = 0.9365 g/ml$$

Hence,

$$\rho_{15}^{15} = \rho_4^{20} + 5\alpha = 0.9365 + 5 \times 0.000594 = 0.9395 g/ml$$

.

Density of Mixed Heavy Crude,

$$\rho_{20}^{4} = 0.9386 g/ml$$

Hence,

$$\rho_{15}^{15} = \rho_4^{20} + 5\alpha = 0.9386 + 5 \times 0.000594 = 0.9416 g/ml$$

Density of Antan Heavy Crude,

$$\rho_{20}^{4} = 0.8995 g/ml$$

Hence,

$$\rho_{15}^{15} = \rho_4^{20} + 5\alpha = 0.8995 + 5 \times 0.000647 = 0.9027 g/ml$$

Therefore,

API gravity of the Venezuela heavy crude is expressed as,

$$API\ gravity = \frac{141.5}{0.9395} - 131.5 = 19.11$$

Similarly,

API gravity of the Mixed heavy crude is expressed as,

$$API\ gravity = \frac{141.5}{0.9416} - 131.5 = 18.78$$

And also,

API gravity of the Antan heavy crude is expressed as,

$$API\ gravity = \frac{141.5}{0.9027} - 131.5 = 25.25$$

- ✓ **For Venezuela Heavy Crude Oil Blends**

From the relationship,

$$d = {}^{6000}/_{\rho s}$$

Where, d is the average particle diameter of crude, S is the specific surface area, which is given as,

$$S = 8.08\ x\ 10^3 B$$ **(Mohammed, 2001)**

And B as coefficient given as,

$B = (\log D_1 - \log D_2) / (\lambda_2 - \lambda_1)$,

Where, D_1 is the absorbance at wavelength, λ_1=580nm and D_2 is the absorbance at wavelength, λ_2=620nm

<u>For 0% UEO Blend</u>

$D_1 = 0.773$, and $D_2 = 0.501$

$B = (\log 0.773 - \log 0.501)/ 40\ x10^{-9} = 4.73\ x\ 10^6$

Therefore,

$S = 8.08\ x\ 10^3\ x\ 4.73\ x\ 10^6 = 3.808\ x\ 10^{10}$ and

$d = 6000/(939.5\ x\ 3.808x10^{10}) = 1.6718x10^{-10}$m

<u>For 1% UEO Blend</u>

$D_1 = 0.486$, and $D_2 = 0.355$

$B = (\log 0.486 - \log 0.355)/ 40\ x10^{-9} = 3.41x\ 10^6$

Therefore,

$S = 8.08\ x\ 10^3\ x\ 3.41\ x\ 10^6 = 2.755\ x\ 10^{10}$ and

$d = 6000/(939.5\ x\ 2.755x10^{10}) = 2.3181x10^{-10}$m

<u>For 2% UEO Blend</u>

$D_1 = 0.570$, and $D_2 = 0.409$

$B = (\log 0.570 - \log 0.409)/ 40\ x10^{-9} = 3.60\ x\ 10^6$

Therefore,

$S = 8.08\ x\ 10^3\ x\ 3.60\ x\ 10^6 = 2.9088\ x\ 10^{10}$ and

$d = 6000/(939.5\ x\ 2.9088\ x10^{10}) = 2.1962\ x\ 10^{-10}$m

For 3% UEO Blend

D_1 = 0.609, and D_2 = 0.440

B = (log 0.609 – log 0.440)/ 40 x10^{-9} =3.53x 10^6

Therefore,

S = 8.08 x 10^3 x 3.53 x 10^6 = 2.852 x 10^{10} and

d= 6000/(939.5 x 2.852 x10^{10}) = 2.2388 x 10^{-10}m

For 4% UEO Blend

D_1 = 0.418, and D_2 = 0.299

B = (log 0.418 – log 0.299)/ 40 x10^{-9} =2.637 x 10^6

Therefore,

S = 8.08 x 10^3 x 2.637 x 10^6 = 2.939 x 10^{10} and

d= 6000/(939.5 x 2.939 x10^{10}) = 2.1738 x 10^{-10}m

For 5% UEO Blend

D_1 = 0.490, and D_2 = 0.354

B = (log 0.490 – log 0.354)/ 40 x10^{-9} =3.53x 10^6

Therefore,

S = 8.08 x 10^3 x 3.53 x 10^6 = 2.852 x 10^{10} and

d= 6000/(939.5 x 2.852 x10^{10}) = 2.2398 x 10^{-10}m

For 6% UEO Blend

D_1 = 0.405, and D_2 = 0.287

B = (log 0.405 – log 0.287)/ 40 x10^{-9} =3.739x 10^6

Therefore,

S = 8.08 x 10^3 x 3.739 x 10^6 = 3.0211 x 10^{10} and

d= 6000/(939.5 x 2.939 x10^{10}) = 2.114 x 10^{-10}m

For 7% UEO Blend

D_1 = 0.443, and D_2 = 0.32

B = (log 0.443 – log 0.32)/ 40 x10^{-9} =3.531x 10^6

Therefore,

S = 8.08 x 10^3 x 3.531 x 10^6 = 2.8533 x 10^{10} and

d= 6000/(939.5 x 2.8533 x10^{10})= 2.2468 x 10^{-10}m

For 8% UEO Blend

D_1 = 0.435, and D_2 = 0.309

B = (log 0.435 – log 0.309)/ 40 $x10^{-9}$ =3.7133 $x\ 10^6$

Therefore,

S = 8.08 $x\ 10^3$ x 3.7133 $x\ 10^6$ = 3.0 $x\ 10^{10}$ and

d= 6000/(939.5 x 3.0 $x10^{10}$) = 2.1286 $x\ 10^{-10}$m

<u>For 9% UEO Blend</u>

D_1 = 0.446, and D_2 = 0.317

B = (log 0.446 – log 0.317)/ 40 $x10^{-9}$ =3.7069 $x\ 10^6$

Therefore,

S = 8.08 $x\ 10^3$ x 3.7069 $x\ 10^6$ = 2.995 $x\ 10^{10}$ and

d= 6000/(939.5 x 2.995 $x10^{10}$) = 2.1323 $x\ 10^{-10}$m

<u>For 10% UEO Blend</u>

D_1 = 0.388, and D_2 = 0.275

B = (log 0.388 – log 0.275)/ 40 $x10^{-9}$ =3.737x 10^6

Therefore,

S = 8.08 $x\ 10^3$ x 3.737 $x\ 10^6$ = 3.0199 $x\ 10^{10}$ and

d= 6000/(939.5 x 3.0199 $x10^{10}$) = 2.1147 $x\ 10^{-10}$m

<u>For 11% UEO Blend</u>

D_1 = 0.496, and D_2 = 0.353

B = (log 0.496 – log 0.353)/ 40 $x10^{-9}$ =3.6927 $x\ 10^6$

Therefore,

S = 8.08 $x\ 10^3$ x 3.6927 $x\ 10^6$ = 2.9837 $x\ 10^{10}$ and

d= 6000/(939.5 x 2.9837$x10^{10}$)= 2.1404 $x10^{-10}$m

<u>For 12% UEO Blend</u>

D_1 = 0.397, and D_2 = 0.281

B = (log 0.397 – log 0.281)/ 40 $x10^{-9}$ =3.7521 $x\ 10^6$

Therefore,

S = 8.08 $x\ 10^3$ x 3.7521 $x\ 10^6$ = 3.0317 $x\ 10^{10}$ and

d= 6000/(939.5 x 3.0317 $x10^{10}$) = 2.1065 $x\ 10^{-10}$m

<u>For 13% UEO Blend</u>

D_1 = 0.586, and D_2 = 0.421

B = (log 0.586 – log 0.421)/ 40 x10^{-9} =3.5904 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.5904 x 10^{6} = 2.901 x 10^{10} and

d= 6000/(939.5 x 2.901 x10^{10}) = 2.2014 x 10^{-10}m

<u>For 14% UEO Blend</u>

D_1 = 0.472, and D_2 = 0.337

B = (log 0.472 – log 0.337)/ 40 x10^{-9} =3.6578 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6578 x 10^{6} = 2.9555 x 10^{10} and

d= 6000/(939.5 x 2.9555 x10^{10}) = 2.1609 x 10^{-10}m

<u>For 15% UEO Blend</u>

D_1 = 0.652, and D_2 = 0.470

B = (log 0.652 – log 0.470)/ 40 x10^{-9} =3.5537 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.5537 x 10^{6} = 2.8714 x 10^{10} and

d= 6000/(939.5 x 2.8714 x10^{10}) = 2.2241 x 10^{-10}m

<u>For 16% UEO Blend</u>

D_1 = 0.367, and D_2 = 0.264

B = (log 0.367 – log 0.264)/ 40 x10^{-9} =3.5766x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.5766 x 10^{6} = 2.8899 x 10^{10} and

d= 6000/(939.5 x 2.8899 x10^{10}) = 2.2098 x 10^{-10}m

<u>For 17% UEO Blend</u>

D_1 = 0.362, and D_2 = 0.259

B = (log 0.362 – log 0.259)/ 40 x10^{-9} =3.6352x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6352 x 10^{6} = 2.9373 x 10^{10} and

d= 6000/(939.5 x 2.9373 x10^{10}) = 2.1742 x 10^{-10}m

<u>For 18% UEO Blend</u>

D_1 = 0.371, and D_2 = 0.264

B = (log 0.371 – log 0.264)/ 40 x10^{-9} =3.6942 x 10^{6}

Therefore,

$S = 8.08 \times 10^3 \times 3.6942 \times 10^6 = 2.985 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.985 \times 10^{10}) = 2.1395 \times 10^{-10}$m

<u>For 19% UEO Blend</u>

$D_1 = 0.481$, and $D_2 = 0.345$

$B = (\log 0.481 - \log 0.345)/ 40 \times 10^{-9} = 3.608 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.608 \times 10^6 = 2.9154 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.9154 \times 10^{10}) = 2.1906 \times 10^{-10}$m

<u>For 20% UEO Blend</u>

$D_1 = 0.417$, and $D_2 = 0.300$

$B = (\log 0.417 - \log 0.300)/ 40 \times 10^{-9} = 3.5754 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5754 \times 10^6 = 2.8889 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.8889 \times 10^{10}) = 2.2106 \times 10^{-10}$m

<u>For 21% UEO Blend</u>

$D_1 = 0.387$, and $D_2 = 0.276$

$B = (\log 0.387 - \log 0.276)/ 40 \times 10^{-9} = 3.67 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.67 \times 10^6 = 2.9654 \times 10^{10}$ and

$d = 6000/(936.5 \times 2.9654 \times 10^{10}) = 2.1536 \times 10^{-10}$m

<u>For 22% UEO Blend</u>

$D_1 = 0.397$, and $D_2 = 0.284$

$B = (\log 0.397 - \log 0.284)/ 40 \times 10^{-9} = 3.6368 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.6368 \times 10^6 = 2.9385 \times 10^{10}$ and

$d = 6000/(936.5 \times 2.9385 \times 10^{10}) = 2.1733 \times 10^{-10}$m

<u>For 23% UEO Blend</u>

$D_1 = 0.530$, and $D_2 = 0.381$

$B = (\log 0.530 - \log 0.381)/ 40 \times 10^{-9} = 3.5838 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5838 \times 10^6 = 2.8957 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.8957 \times 10^{10}) = 2.2054 \times 10^{-10}$m

<u>For 24% UEO Blend</u>

$D_1 = 0.487$, and $D_2 = 0.348$

$B = (\log 0.487 - \log 0.348)/ 40 \times 10^{-9} = 3.6487 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 2.6487 \times 10^6 = 2.9482 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.9482 \times 10^{10}) = 2.1662 \times 10^{-10}$m

<u>For 25% UEO Blend</u>

$D_1 = 0.433$, and $D_2 = 0.313$

$B = (\log 0.433 - \log 0.313)/ 40 \times 10^{-9} = 3.5236 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5236 \times 10^6 = 2.8471 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.8471 \times 10^{10}) = 2.2431 \times 10^{-10}$m

<u>For 26% UEO Blend</u>

$D_1 = 0.582$, and $D_2 = 0.421$

$B = (\log 0.582 - \log 0.421)/ 40 \times 10^{-9} = 3.5160 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5160 \times 10^6 = 2.8409 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.8409 \times 10^{10}) = 2.248 \times 10^{-10}$m

<u>For 27% UEO Blend</u>

$D_1 = 0.515$, and $D_2 = 0.369$

$B = (\log 0.515 - \log 0.369)/ 40 \times 10^{-9} = 3.6195 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.6195 \times 10^6 = 2.9246 \times 10^{10}$ and

$d = 6000/(939.5 \times 2.9246 \times 10^{10}) = 2.1837 \times 10^{-10}$m

<u>For 28% UEO Blend</u>

$D_1 = 0.521$, and $D_2 = 0.376$

$B = (\log 0.521 - \log 0.376)/ 40 \times 10^{-9} = 3.5412 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5412 \times 10^6 = 2.8613 \times 10^{10}$ and

d= 6000/(939.5 x 2.8613 x10^{10}) = 2.232 x 10^{-10}m

<u>For 29% UEO Blend</u>

D_1 = 0.425, and D_2 = 0.304

B = (log 0.425 – log 0.304)/ 40 x10^{-9} =3.6379 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6379 x 10^{6} = 2.939 x 10^{10} and

d= 6000/(939.5 x 2.939 x10^{10}) = 2.132 x 10^{-10}m

<u>For 30% UEO Blend</u>

D_1 = 0.385, and D_2 = 0.277

B = (log 0.385 – log 0.277)/ 40 x10^{-9} =3.5745x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.5745 x 10^{6} = 2.8882 x 10^{10} and

d= 6000/(939.5 x 2.8882 x10^{10}) = 2.2112 x 10^{-10}m

- ✓ **For Mixed Heavy Crude Oil Blends**

<u>For 0% UEO Blend</u>

D_1 = 0.518, and D_2 = 0.431

B = (log 0.518 – log 0.431)/ 40 x10^{-9} =3.4425 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.4425 x 10^{6} = 2.052 x 10^{10} and

d= 6000/(941.6 x 2.052x10^{10}) = 2.08 x10^{-10}m

<u>For 1% UEO Blend</u>

D_1 = 0.445, and D_2 = 0.317

B = (log 0.445 – log 0.317)/ 40 x10^{-9} =3.6825 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6825 x 10^{6} = 2.9755 x 10^{10} and

d= 6000/(941.6 x 2.9755x10^{10}) = 2.1412 x10^{-10}m

<u>For 2% UEO Blend</u>

D_1 = 0.391, and D_2 = 0.278

B = (log 0.391 – log 0.278)/ 40 x10^{-9} =3.7033 x 10^{6}

Therefore,

$S = 8.08 \times 10^3 \times 3.7033 \times 10^6 = 2.992 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.992 \times 10^{10}) = 2.1293 \times 10^{-10}$m

<u>For 3% UEO Blend</u>

$D_1 = 0.365$, and $D_2 = 0.260$

$B = (\log 0.365 - \log 0.260)/ 40 \times 10^{-9} = 3.683 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.683 \times 10^6 = 2.9759 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9759 \times 10^{10}) = 2.141 \times 10^{-10}$m

<u>For 4% UEO Blend</u>

$D_1 = 0.343$, and $D_2 = 0.243$

$B = (\log 0.343 - \log 0.243)/ 40 \times 10^{-9} = 3.742 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.742 \times 10^6 = 3.021 \times 10^{10}$ and

$d = 6000/(941.6 \times 3.021 \times 10^{10}) = 2.110 \times 10^{-10}$m

<u>For 5% UEO Blend</u>

$D_1 = 0.429$, and $D_2 = 0.305$

$B = (\log 0.429 - \log 0.305)/ 40 \times 10^{-9} = 3.5977 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5977 \times 10^6 = 2.9069 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9069 \times 10^{10}) = 2.1917 \times 10^{-10}$m

<u>For 6% UEO Blend</u>

$D_1 = 0.418$, and $D_2 = 0.297$

$B = (\log 0.418 - \log 0.297)/ 40 \times 10^{-9} = 3.7105 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.7105 \times 10^6 = 2.9981 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9981 \times 10^{10}) = 2.1252 \times 10^{-10}$m

<u>For 7% UEO Blend</u>

$D_1 = 0.33$, and $D_2 = 0.24$

$B = (\log 0.33 - \log 0.24)/ 40 \times 10^{-9} = 3.4576 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.4576 \times 10^6 = 2.7937 \times 10^{10}$ and

d= 6000/(941.6 x 2.7937 x10^{10}) = 2.2807 x 10^{-10}m

For 8% UEO Blend

D_1 = 0.450, and D_2 = 0.322

B = (log 0.450 – log 0.322)/ 40 x10^{-9} =3.6339 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6339 x 10^{6} = 2.9362 x 10^{10} and

d= 6000/(941.6 x 2.9362 x10^{10}) = 2.1699 x 10^{-10}m

For 9% UEO Blend

D_1 = 0.375, and D_2 = 0.268

B = (log 0.375 – log 0.268)/ 40 x10^{-9} =3.6474 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6474 x 10^{6} = 2.9471 x 10^{10} and

d= 6000/(941.6 x 2.9471 x10^{10}) = 2.162 x 10^{-10}m

For 10% UEO Blend

D_1 = 0.459, and D_2 = 0.33

B = (log 0.459 – log 0.33)/ 40 x10^{-9} =3.5852x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.5852 x 10^{6} = 2.8946 x 10^{10} and

d= 6000/(941.6 x 2.8946 x10^{10}) = 2.2011 x 10^{-10}m

For 11% UEO Blend

D_1 = 0.322, and D_2 = 0.231

B = (log 0.322 – log 0.231)/ 40 x10^{-9} =3.6061 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6061 x 10^{6} = 2.9137 x 10^{10} and

d= 6000/(941.6 x 2.9137x10^{10}) = 2.1867 x10^{-10}m

For 12% UEO Blend

D_1 = 0.282, and D_2 = 0.202

B = (log 0.282 – log 0.202)/ 40 x10^{-9} =3.6224 x 10^{6}

Therefore,

S = 8.08 x 10^{3} x 3.6224 x 10^{6} = 2.9269 x 10^{10} and

d= 6000/(941.6 x 2.9269 x10^{10}) = 2.1768 x 10^{-10}m

For 13% UEO Blend

D_1 = 0.341, and D_2 = 0.244

B = (log 0.341 – log 0.244)/ 40 x10^{-9} =3.6341 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.6341 x 10^6 = 2.9364 x 10^{10} and

d= 6000/(941.6 x 2.9364 x10^{10}) = 2.1698 x 10^{-10}m

For 14% UEO Blend

D_1 = 0.368, and D_2 = 0.262

B = (log 0.368 – log 0.262)/ 40 x10^{-9} =3.6887 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.6887 x 10^6 = 2.9804 x 10^{10} and

d= 6000/(941.6 x 2.9804 x10^{10}) = 2.1377 x 10^{-10}m

For 15% UEO Blend

D_1 = 0.306, and D_2 = 0.220

B = (log 0.306 – log 0.220)/ 40 x10^{-9} =3.5825 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.5825 x 10^6 = 2.8946 x 10^{10} and

d= 6000/(941.6 x 2.8946 x10^{10}) = 2.2011 x 10^{-10}m

For 16% UEO Blend

D_1 = 0.349, and D_2 = 0.257

B = (log 0.349 – log 0.257)/ 40 x10^{-9} =3.3223 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.3223 x 10^6 = 2.6844 x 10^{10} and

d= 6000/(941.6 x 2.6844 x10^{10}) = 2.3734 x 10^{-10}m

For 17% UEO Blend

D_1 = 0.252, and D_2 = 0.179

B = (log 0.252 – log 0.179)/ 40 x10^{-9} =3.7137 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.7137 x 10^6 = 3.0007 x 10^{10} and

d= 6000/(941.6 x 3.0007 x10^{10}) = 2.1234 x 10^{-10}m

For 18% UEO Blend

D_1 = 0.278, and D_2 = 0.202

B = (log 0.278 – log 0.202)/ 40 $x10^{-9}$ =3.5754 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.5754 x 10^6 = 2.8889 x 10^{10} and

d= 6000/(941.6 x 2.8889 $x10^{10}$) = 2.2055 x 10^{-10}m

<u>For 19% UEO Blend</u>

D_1 = 0.305, and D_2 = 0.219

B = (log 0.305 – log 0.219)/ 40 $x10^{-9}$ =3.5964 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.5964 x 10^6 = 2.9059 x 10^{10} and

d= 6000/(941.6 x 2.9059 $x10^{10}$) = 2.1926 x 10^{-10}m

<u>For 20% UEO Blend</u>

D_1 = 0.409, and D_2 = 0.293

B = (log 0.409 – log 0.293)/ 40 $x10^{-9}$ =3.6214 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.6214 x 10^6 = 2.9261 x 10^{10} and

d= 6000/(941.6 x 2.9261 $x10^{10}$) = 2.1775 x 10^{-10}m

<u>For 21% UEO Blend</u>

D_1 = 0.357, and D_2 = 0.256

B = (log 0.357 – log 0.256)/ 40 $x10^{-9}$ =3.6107 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.6107 x 10^6 = 2.9175 x 10^{10} and

d= 6000/(941.6 x 2.9175$x10^{10}$) = 2.1839 x 10^{-10}m

<u>For 22% UEO Blend</u>

D_1 = 0.326, and D_2 = 0.234

B = (log 0.326 – log 0.234)/ 40 $x10^{-9}$ =3.6 x 10^6

Therefore,

S = 8.08 x 10^3 x 3.6 x 10^6 = 2.9088 x 10^{10} and

d= 6000/(941.6 x 2.9088 $x10^{10}$) = 2.1904 x 10^{-10}m

<u>For 23% UEO Blend</u>

D_1 = 0.338, and D_2 = 0.246

$B = (\log 0.338 - \log 0.246)/ 40 \times 10^{-9} = 3.4495 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^{3} \times 3.4495 \times 10^{6} = 2.7872 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.7872 \times 10^{10}) = 2.2221 \times 10^{-10}$m

<u>For 24% UEO Blend</u>

$D_1 = 0.217$, and $D_2 = 0.159$

$B = (\log 0.217 - \log 0.159)/ 40 \times 10^{-9} = 3.3766 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^{3} \times 3.3766 \times 10^{6} = 2.7283 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.7283 \times 10^{10}) = 2.3354 \times 10^{-10}$m

<u>For 25% UEO Blend</u>

$D_1 = 0.386$, and $D_2 = 0.277$

$B = (\log 0.386 - \log 0.277)/ 40 \times 10^{-9} = 3.6027 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^{3} \times 3.6027 \times 10^{6} = 2.911 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.911 \times 10^{10}) = 2.1888 \times 10^{-10}$m

<u>For 26% UEO Blend</u>

$D_1 = 0.347$, and $D_2 = 0.248$

$B = (\log 0.347 - \log 0.248)/ 40 \times 10^{-9} = 3.6469 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^{3} \times 3.6469 \times 10^{6} = 2.9467 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9467 \times 10^{10}) = 2.1622 \times 10^{-10}$m

<u>For 27% UEO Blend</u>

$D_1 = 0.357$, and $D_2 = 0.256$

$B = (\log 0.357 - \log 0.256)/ 40 \times 10^{-9} = 3.6107 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^{3} \times 3.6107 \times 10^{6} = 2.9175 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9175 \times 10^{10}) = 2.1839 \times 10^{-10}$m

<u>For 28% UEO Blend</u>

$D_1 = 0.366$, and $D_2 = 0.263$

$B = (\log 0.366 - \log 0.263)/ 40 \times 10^{-9} = 3.5881 \times 10^{6}$

Therefore,

$S = 8.08 \times 10^3 \times 3.5881 \times 10^6 = 2.8992 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.8991 \times 10^{10}) = 2.1976 \times 10^{-10}$m

<u>For 29% UEO Blend</u>

$D_1 = 0.305$, and $D_2 = 0.219$

$B = (\log 0.305 - \log 0.219)/ 40 \times 10^{-9} = 3.5964 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.5964 \times 10^6 = 2.9059 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9059 \times 10^{10}) = 2.1926 \times 10^{-10}$m

<u>For 30% UEO Blend</u>

$D_1 = 0.249$, and $D_2 = 0.177$

$B = (\log 0.249 - \log 0.177)/ 40 \times 10^{-9} = 3.7047 \times 10^6$

Therefore,

$S = 8.08 \times 10^3 \times 3.7047 \times 10^6 = 2.9942 \times 10^{10}$ and

$d = 6000/(941.6 \times 2.9942 \times 10^{10}) = 2.1279 \times 10^{-10}$m

- ✓ **For Antan Heavy Crude Oil Blends**

<u>For 0% UEO Blend</u>

$D_1 = 0.988$, and $D_2 = 0.702$

$B = (\log 0.988 - \log 0.702)/ 40 \times 10^{-9} = 2.71 \times 10^6$

$S = 8.08 \times 10^3 \times 2.71 \times 10^6 = 3.0 \times 10^{10}$

$d = 6000/ (902.7 \times 3.0 \times 10^{10}) = 2.216 \times 10^{-10}$m

<u>For 1% UEO BLEND</u>

$D_1 = 0.957$, and $D_2 = 0.715$

$B = (\log 0.957 - \log 0.715)/ 40 \times 10^{-9} = 3.165 \times 10^6$

$S = 8.08 \times 10^3 \times 3.165 \times 10^6 = 2.557 \times 10^{10}$

$d = 6000/ (902.7 \times 2.557 \times 10^{10}) = 2.599 \times 10^{-10}$m

<u>For 2% UEO BLEND</u>

$D_1 = 0.789$, and $D_2 = 0.591$

$B = (\log 0.789 - \log 0.591)/ 40 \times 10^{-9} = 3.137 \times 10^6$

$S = 8.08 \times 10^3 \times 3.137 \times 10^6 = 2.535 \times 10^{10}$

$d = 6000/ (902.7 \times 2.535 \times 10^{10}) = 2.622 \times 10^{-10}$m

For 3% UEO BLEND

$D_1 = 0.863$, and $D_2 = 0.659$

$B = (\log 0.863 - \log 0.659)/ 40 \times 10^{-9} = 2.93 \times 10^6$

$S = 8.08 \times 10^3 \times 2.93 \times 10^6 = 2.367 \times 10^{10}$

$d = 6000/ (902.7 \times 2.367 \times 10^{10}) = 2.8 \times 10^{-10}$m

For 4% UEO BLEND

$D_1 = 0.833$, and $D_2 = 0.623$

$B = (\log 0.833 - \log 0.623)/ 40 \times 10^{-9} = 3.154 \times 10^6$

$S = 8.08 \times 10^3 \times 3.154 \times 10^6 = 2.55 \times 10^{10}$

$d = 6000/ (902.7 \times 2.55 \times 10^{10}) = 2.606 \times 10^{-10}$m

For 5% UEO BLEND

$D_1 = 0.888$, and $D_2 = 0.668$

$B = (\log 0.888 - \log 0.688)/ 40 \times 10^{-9} = 3.091 \times 10^6$

$S = 8.08 \times 10^3 \times 3.091 \times 10^6 = 2.498 \times 10^{10}$

$d = 6000/ (902.7 \times 2.498 \times 10^{10}) = 2.660 \times 10^{-10}$m

For 6% UEO BLEND

$D_1 = 0.788$, and $D_2 = 0.589$

$B = (\log 0.788 - \log 0.589)/ 40 \times 10^{-9} = 3.16 \times 10^6$

$S = 8.08 \times 10^3 \times 3.16 \times 10^6 = 2.553 \times 10^{10}$

$d = 6000/ (902.7 \times 2.553 \times 10^{10}) = 2.609 \times 10^{-10}$m

For 7% UEO BLEND

$D_1 = 0.708$, and $D_2 = 0.52$

$B = (\log 0.708 - \log 0.52)/ 40 \times 10^{-9} = 3.35 \times 10^6$

$S = 8.08 \times 10^3 \times 3.35 \times 10^6 = 2.708 \times 10^{10}$

$d = 6000/ (902.7 \times 2.708 \times 10^{10}) = 2.454 \times 10^{-10}$m

For 8% UEO BLEND

$D_1 = 0.795$, and $D_2 = 0.587$

$B = (\log 0.795 - \log 0.587)/ 40 \times 10^{-9} = 3.29 \times 10^6$

$S = 8.08 \times 10^3 \times 3.29 \times 10^6 = 2.65 \times 10^{10}$

$d = 6000/ (902.7 \times 2.65 \times 10^{10}) = 2.508 \times 10^{-10} m$

For 9% UEO BLEND

$D_1 = 0.775$, and $D_2 = 0.589$

$B = (\log 0.775 - \log 0.589)/ 40 \times 10^{-9} = 2.98 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 2.98 \times 10^{6} = 2.408 \times 10^{10}$

$d = 6000/ (902.7 \times 2.408 \times 10^{10}) = 2.760 \times 10^{-10} m$

For 10% UEO BLEND

$D_1 = 0.764$, and $D_2 = 0.574$

$B = (\log 0.764 - \log 0.574)/ 40 \times 10^{-9} = 3.105 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 3.105 \times 10^{6} = 2.51 \times 10^{10}$

$d = 6000/ (902.7 \times 2.51 \times 10^{10}) = 2.648 \times 10^{-10} m$

For 11% UEO BLEND

$D_1 = 0.282$, and $D_2 = 0.236$

$B = (\log 0.282 - \log 0.236)/ 40 \times 10^{-9} = 1.933 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 1.933 \times 10^{6} = 1.56 \times 10^{10}$

$d = 6000/ (902.7 \times 1.56 \times 10^{10}) = 4.26 \times 10^{-10} m$

For 12% UEO BLEND

$D_1 = 0.753$, and $D_2 = 0.568$

$B = (\log 0.753 - \log 0.568)/ 40 \times 10^{-9} = 3.061 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 3.061 \times 10^{6} = 2.473 \times 10^{10}$

$d = 6000/ (902.7 \times 2.473 \times 10^{10}) = 2.688 \times 10^{-10} m$

For 13% UEO BLEND

$D_1 = 0.778$, and $D_2 = 0.589$

$B = (\log 0.778 - \log 0.589)/ 40 \times 10^{-9} = 3.02 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 3.02 \times 10^{6} = 2.44 \times 10^{10}$

$d = 6000/ (902.7 \times 2.44 \times 10^{10}) = 2.72 \times 10^{-10} m$

For 14% UEO BLEND

$D_1 = 0.187$, and $D_2 = 0.165$

$B = (\log 0.187 - \log 0.165)/ 40 \times 10^{-9} = 1.359 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 1.359 \times 10^{6} = 1.098 \times 10^{10}$

$d = 6000/ (902.7 \times 1.098 \times 10^{10}) = 6.054 \times 10^{-10} m$

For 15% UEO BLEND

D_1 = 0.802, and D_2 = 0.604

B = (log 0.802 – log 0.604)/ 40 $x10^{-9}$ = 3.078 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.078 $x10^{6}$ = 2.487 $x10^{10}$

d = 6000/ (902.7 x 2.487 $x10^{10}$) = 2.672 $x10^{-10}$m

For 16% UEO BLEND

D_1 = 0.665, and D_2 = 0.493

B = (log 0.665 – log 0.493)/ 40 $x10^{-9}$ = 3.249 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.249 $x10^{6}$ = 2.625 $x10^{10}$

d = 6000/ (902.7 x 2.625 $x10^{10}$) = 2.532 $x10^{-10}$m

For 17% UEO BLEND

D_1 = 0.704, and D_2 = 0.527

B = (log 0.704 – log 0.527)/ 40 $x10^{-9}$ = 3.144 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.144 $x10^{6}$ = 2.54 $x10^{10}$

d = 6000/ (902.7 x 2.54 $x10^{10}$) = 2.616 $x10^{-10}$m

For 18% UEO BLEND

D_1 = 0.666, and D_2 = 0.492

B = (log 0.666 – log 0.492)/ 40 $x10^{-9}$ = 3.288 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.288 $x10^{6}$ = 2.657 $x10^{10}$

d = 6000/ (902.7 x 2.657 $x10^{10}$) = 2.501 $x10^{-10}$m

For 19% UEO BLEND

D_1 = 0.171, and D_2 = 0.153

B = (log 0.171 – log 0.153)/ 40 $x10^{-9}$ = 1.2 $x10^{6}$

S = 8.08 $x10^{3}$ x 1.2 $x10^{6}$ = 0.9 $x10^{10}$

d = 6000/ (902.7 x 0.9 $x10^{10}$) = 7.385 $x10^{-10}$m

For 20% UEO BLEND

D_1 = 0.676, and D_2 = 0.505

B = (log 0.676 – log 0.505)/ 40 $x10^{-9}$ = 3.166 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.166 $x10^{6}$ = 2.558 $x10^{10}$

d = 6000/ (902.7 x 2.558 $x10^{10}$) = 2.598 $x10^{-10}$m

For 21% UEO BLEND

D_1 = 0.624, and D_2 = 0.461

B = (log 0.624 – log 0.461)/ 40 $x10^{-9}$ = 3.287$x10^{6}$

S = 8.08 $x10^{3}$ x 3.287 $x10^{6}$ = 2.655 $x10^{10}$

d = 6000/ (902.7 x 2.655 $x10^{10}$) = 2.503 $x10^{-10}$m

For 22% UEO BLEND

D_1 = 0.138, and D_2 = 0.123

B = (log 0.138 – log 0.123)/ 40 $x10^{-9}$ = 1.249 $x10^{6}$

S = 8.08 $x10^{3}$ x 1.429 $x10^{6}$ = 1.01 $x10^{10}$

d = 6000/ (902.7 x 1.01 $x10^{10}$) = 6.58 $x10^{-10}$m

For 23% UEO BLEND

D_1 = 0.916, and D_2 = 0.753

B = (log 0.916 – log 0.753)/ 40 $x10^{-9}$ = 2.13 $x10^{6}$

S = 8.08 $x10^{3}$ x 2.13 $x10^{6}$ = 1.72 $x10^{10}$

d = 6000/ (902.7 x 1.72 $x10^{10}$) = 3.864 $x10^{-10}$m

For 24% UEO BLEND

D_1 = 0.752, and D_2 = 0.568

B = (log 0.752 – log 0.568)/ 40 $x10^{-9}$ = 3.047 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.047 $x10^{6}$ = 2.46 $x10^{10}$

d = 6000/ (902.7 x 2.46 $x10^{10}$) = 2.702 $x10^{-10}$m

For 25% UEO BLEND

D_1 = 0.790, and D_2 = 0.596

B = (log 0.790 – log 0.596)/ 40 $x10^{-9}$ = 3.06 $x10^{6}$

S = 8.08 $x10^{3}$ x 3.06 $x10^{6}$ = 2.47 $x10^{10}$

d = 6000/ (902.7 x 2.47 $x10^{10}$) = 2.69 $x10^{-10}$m

For 26% UEO BLEND

D_1 = 0.140, and D_2 = 0.123

B = (log 0.140 – log 0.123)/ 40 $x10^{-9}$ = 1.41 $x10^{6}$

S = 8.08 $x10^{3}$ x 1.41 $x10^{6}$ = 1.136 $x10^{10}$

d = 6000/ (902.7 x 1.136 $x10^{10}$) = 5.85 $x10^{-10}$m

For 27% UEO BLEND

D_1 = 0.475, and D_2 = 0.354

$B = (\log 0.475 - \log 0.354)/ 40 \times 10^{-9} = 3.192 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 3.192 \times 10^{6} = 2.58 \times 10^{10}$

$d = 6000/ (902.7 \times 2.58 \times 10^{10}) = 2.58 \times 10^{-10}$m

<u>For 28% UEO BLEND</u>

$D_1 = 0.712$, and $D_2 = 0.538$

$B = (\log 0.712 - \log 0.538)/ 40 \times 10^{-9} = 3.04 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 3.04 \times 10^{6} = 2.458 \times 10^{10}$

$d = 6000/ (902.7 \times 2.458 \times 10^{10}) = 2.704 \times 10^{-10}$m

<u>For 29% UEO BLEND</u>

$D_1 = 0.641$, and $D_2 = 0.489$

$B = (\log 0.641 - \log 0.489)/ 40 \times 10^{-9} = 2.94 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 2.94 \times 10^{6} = 2.37 \times 10^{10}$

$d = 6000/ (902.7 \times 2.37 \times 10^{10}) = 2.804 \times 10^{-10}$m

<u>For 30% UEO BLEND</u>

$D_1 = 0.669$, and $D_2 = 0.508$

$B = (\log 0.669 - \log 0.508)/ 40 \times 10^{-9} = 2.99 \times 10^{6}$

$S = 8.08 \times 10^{3} \times 2.99 \times 10^{6} = 2.415 \times 10^{10}$

$d = 6000/ (902.7 \times 2.47 \times 10^{10}) = 2.752 \times 10^{-10}$m